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EVALUATION AND MODIFICATION OF FLUORIDE SAMPLING AND ANALYTICAL METHODS

Robert S. Sholtes, et al

Environmental Science and Engineering, Incorporated

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16. Abstracts The original project was to evaluate the Arthur D. Little Method by comparison with the Inter-Society Committee Method for steam distillation from perchloric acid, using field and laboratory samples. Subsequently, the work was reoriented towards primary evaluation of the Decker method and, later, the EPA method 13 (similar to Decker). The fluoride measurement methods are described and the results compared. The parameters of the fluoride determination method are as follows: distillation type, acid, temperature and measurement mode (SPADNS or electrode). Three sampling trains were tested, evaluated and illustrated. The basic design considerations to develop a continuous fluoride source monitor are presented. Some of the results and conclusions are as follows: (1) the EPA No. 13 fluoride method can give results on comparative tests that are within five percent; (2) in the concentration range of 10-100 ppm F^-, the average collection efficiency of the EPA train using water was 58 percent; using 0.1N Nu OH, it was 77 percent; ar. (3) measurements by both the electrode and SPADNS on a set of triple superphosphate plant samples indicated that the two modes were essentially equivalent. Numerous other conclusions and recommendations are given. The three methods are appended to this report.

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TABLE OF CONTENTS

	Page
List of Tables	ii
List of Figures	iv
Acknowledgements	v
Section I - Conclusions	1
Section II - Recommendations	3
Section III - 1.0 Introduction	4
2.0 Methods Review	5
3.0 Laboratory Activities	11
4.0 Field Activities	59
5.0 Collection Efficiency Study	65
6.0 Continuous Fluoride Monitor	79
Appendixes	86

LIST OF TABLES

		Page
1.	A COMPARISON OF FLUORIDE DETERMINATION METHOD PARAMETERS	9
2.	RECOVERY OF FLUORIDE USING DIRECT DISTILLATION FROM SULFURIC ACID at 210°C.	12
3.	PRELIMINARY WATER SOLUBLE FLUORIDES ANALYSIS-TRIPLE SUPER PHOSPHATE PLANT	15
4.	RECOVERY OF SODIUM FLUORIDE DISTILLED BY INTERSOCIETY METHOD - PERCHLORIC ACID	17
5.	SODIUM FLUORIDE RECOVERIES AT VARIOUS FINAL TEMPERATURES BY DIRECT SULFURIC ACID DISTILLATION	20
6.	STATISTICS SUMMARY FOR 0.500 mg NONDISTILLED AND DISTILLED FLUORIDE DETERMINATIONS	23
7.	FLUORIDE RECOVERY USING 0.5 mg STANDARD SAMPLES WITH THREE DISTILLATION METHODS AND TWO MEASUREMENT MODES	24
8.	DISTRIBUTION OF RESIDUAL FLUORIDE AMONG STILL COMPONENTS	27
9.	MEASUREMENT STATISTICS FOR STEAM DISTILLED FLUORIDES-SPADNS VERSUS ELECTRODE MEASUREMENT MODES	29
10.	WATER SOLUBLE FLUORIDES SAMPLING PRECISION ANALYSIS - DIAMMONIUM PHOSPHATE PLANT, ADL METHOD	37
11.	WATER SOLUBLE FLUORIDE MEASUREMENTS - TRIPLE SUPERPHOSPHATE PLANT	38
12.	STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS-TRIPLE SUPER PHOSPHATE PLANT	40
13.	WATER SOLUBLE FLUORIDES RELATIVE ANALYSIS PRECISION - DE-FLUORINATION PLANT	42
14.	STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS - DEFLUORINATION PLANT	44
15.	MATRIX INTERFERENCE EFFECT UPON WATER SOLUBLE FLUORIDES MEASUREMENTS - DEFLUORINATION PLANT	45
16.	FLUORIDES STORAGE IN POLYETHYLENE BOTTLES, WITH AND WITHOUT REFRIGERATION AT 45°F - WET PHOSPHORIC ACID PLANT	46

		Page
17.	WATER SOLUBLE FLUORIDES RELATIVE ANALYSIS PRECISION - WET PHOSPHORIC ACID PLANT	48
18.	STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS - WET PHOSPHORIC ACID PLANT	49
19.	MATRIX INTERFERENCE EFFECT UPON WATER SOLUBLE FLUORIDES MEASUREMENTS - WET PHOSPHORIC ACID PLANT	50
20.	SPADNS MEASUREMENTS PRIOR TO AND AFTER DISTILLATION - WET PHOSPHORIC ACID PLANT	51
21.	FLUORIDES STROAGE IN POLYETHYLENE BOTTLES, WITH AND WITHOUT REFIRGERATION AT 45°F - WET PHOSPHORIC ACID PLANT	53
22.	WATER SOLUBLE FLUORIDES RELATIVE ANALYSIS PRECISION - ALUMINUM REDUCTION PLANT	54
23.	STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS - ALUMINUM REDUCTION PLANT	55
24.	TOTAL FLUORIDES MEASUREMENTS CORRECTED FOR 6.2 PERCENT MATRIX INTERFERENCE DEPRESSION - ALUMINUM REDUCTION PLANT	57
25.	FLUORIDES STORAGE IN GLASS AND POLYETHYLENE BOTTLES, WITH AND WITHOUT REFRIGERATION (45°F) - ALUMINUM REDUCTION PLANT	58
26.	FLUORIDE CONCENTRATION SUMMARY	60, 61
27.	COLLECTION EFFICIENCY STUDY FOR HF	69
28.	PERCENT REMAINING FLUORIDE RECOVERED	71
29.	HF COLLECTION EFFICIENCIES	73, 74
30.	FLUORIDE RECOVERIES	78
31.	CONTINUOUS MONITOR FIELD RESULTS	84

LIST OF FIGURES

		Page
1.	EPA METHOD 5 PARTICULATE SAMPLING TRAIN	6, 63
2.	PROPOSED EPA FLUORIDE SAMPLING TRAIN	7, 64
3.	MODIFIED FLORIDA TRAIN	8, 64A
4.	MODEL 801 ORION METER READINGS AS A FUNCTION OF TIME	31
5.	EFFECT OF ELECTRODE MEASUREMENT HISTORY UPON RESPONSE (April 23, 1973) SERIES 1	32
6.	EFFECT OF ELECTRODE MEASUREMENT HISTORY UPON RESPONSE (April 27, 1973) SERIES 2	33
7.	EFFECT OF ELECTRODE MEASUREMENT HISTORY UPON RESPONSE (April 30, 1973) SERIES 3	34
8.	STANDARD NaF ADDITIONS FOR INTERFERENCE AND RELATIVE ERROR DETERMINATIONS - TRIPLE SUPER PHOSPHATE PLANT	41
9.	FIRST EXPERIMENTAL SET-UP FOR COLLECTION EFFICIENCY STUDY	66
10.	SECOND EXPERIMENTAL SET-UP FOR COLLECTION EFFICIENCY STUDY	67
11.	FINAL EXPERIMENTAL SET-UP FOR COLLECTION EFFICIENCY STUDY	72
12.	COLLECTION EFFICIENCY VS CONCENTRATION DISTILLED WATER	75
13.	COLLECTION EFFICIENCY VS CONCENTRATION 0.1 N NaOH	76
14.	CONTINUOUS FLUORIDE MONITOR	80
15.	CONTINUOUS MONITOR CALIBRATION CURVE	83

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The field sampling team was led by Mr. J. D. Riggenbach, assisted by Messrs. M. K. Hamlin, L. V. Wurts and T. E. Boldus.

The continuous fluoride monitor was principally designed by Dr. D. A. Falgout and fabricated by Mr. J. D. Riggenbach.

SECTION I

CONCLUSIONS

With care in placement of the probes and operation of the train, the EPA fluoride method can give results on comparative tests that are within five percent.

Data collected using three EPA fluoride trains simultaneously at field sites indicated that variation between EPA trains can be as good as five percent and as poor as 24 percent. The data are very limited (6 sets of 3 simultaneous tests) and statistical analysis of the results varied. For the three tests conducted at the D.A.P. outlet, the average relative standard deviation was 24 percent; the three tests on the outlet of the aluminum reduction plant had an average relative standard deviation of six percent -- quite a bit better.

In the concentration range of 10 - 100 ppm F^-, the average collection efficiency of the EPA train using water was 58 percent (+19%); using 0.1 N NaOH, it was 77 percent (+23%). However, for two runs at about 100 ppm F^- (referenced in the text), the collection efficiency of a similar train was 90 percent in the range of 0 - 4000 ppm. Statistical analysis of the data indicated no significant difference between water and NaOH as absorbing reagents; nor did analysis reveal differences in collection efficiency at different flow rates (3/4 and 1 CFM).

Statistical analysis comparing the results of the Florida and EPA train indicated no significant difference between the two methods at the 99 percent confidence level. The only exception was on the data from the defluorination kiln scrubber inlet where analysis did reveal a difference at the 99 percent confidence level.

Direct distillation, as recommended by the C.E. Decker and tentative EPA Method 13, had been found unacceptable by virtue of incomplete recovery in the distillation.

Sodium fluoride samples steam distilled (one from perchloric and one from sulfuric acid) by the Intersociety Committee Method[3] resulted in complete recoveries.

A statistical comparison of data for the electrode versus SPADNS methods favored the elctrode by yielding the following averages among four experiments for relative error and relative standard deviations, respectively: Electrode - 8.0 percent and 2.8 percent; SPADNS - 8.9 percent and 4.7 percent.

Fluoride determination sensitivities for the final sulfuric acid distillation temperatures of 180°C, 195°C, and 210°C decreased for the SPADNS measurement mode as .038mg, .075mg, and .144mg, respectively. Electrode sensitivity remained constant at .074mg across the temperature range.

A 10-minute measurement period is necessary to optimize electrode measurement precision.

Measurements by both the electrode and SPADNS on a set of triple superphosphate plant samples indicated that the two modes were essentially equivalent.

Field samples containing fluoride can be stored in polyethylene or glass containers, with or without refrigeration, with significant fluoride loss.

Matrix interference effects for the four plant types studied, as determined by standard additions, ranged from five percent to 16 percent depression.

SECTION II

RECOMMENDATIONS

It is recommended that on further comparative work using large diameter stacks that traverses be made while sampling and alternate parts be utilized when available.

Based on the laboratory study, the following recommendations are submitted relative to the collection efficiency assumptions. Above 100 ppm, the accuracy of the train is ten percent or better. Below this level, the collection efficiency drops off in proportion to the concentrations and can be as poor as 30 percent. The four processes tested during the project all had concentrations less than 100 ppm on the outlets. Care should be taken in such cases in calculating emissions since they could possibly be in error by as much as 70 percent.

Although statistical analysis of the data indicated no significant difference between water and NaOH versus the 50 percent average for water in the range of 10 - 100 ppm prompts some careful consideration. While other investigators have stated that either reagent can be used, they may not have conducted either investigation in this concentration range. Some additional data are needed before a firm recommendation can be made.

Measurements on distilled versus non-distilled wet phosphoric acid plant samples were essentially equivalent. In such cases, matrix interference could be determined directly on undistilled samples and applied to direct measurements on the undistilled samples. A recent (July 6, 1973) publication by Ingvar[6] describes a method for estimating precision for methods of standard addition. Application of Ingvar's method to a particular plant could be used to establish a steady-state matrix interference value for distilled or undistilled samples applied to each plant. The same would apply to determination of relative measurement accuracies which are determined jointly with Matrix interference depression.

The Intersociety Method for sulfuric acid should be evaluated in the future due to its simpler overall method and suitability for use on samples with interferences. The alternate acid, perchloric, is more dangerous for routine use and is not as suitable where interferences are a necessary consideration. The broader fluoride distillation range (0 - 100 mg) would facilitate the attainment of lower relative error when compared to a method that would allow only 0.5 mg fluoride to be distilled.

SECTION III

1.0 INTRODUCTION

With the advent of the promulgation of new source emission standards by the Environmental Protection Agency (EPA), it has become necessary that the agency standardize sampling procedures to determine compliance. Time constraints have limited the amount of evaluation accomplished on those methods which were published initially.

In order to minimize subsequent problems with future published methods, EPA is seeking to examine the methods thoroughly in the laboratory and in the field prior to publication.

By prior contractual arrangements with Arthur D. Little, Inc. (ADL), EPA obtained laboratory-based data on potential manual methods for the determination of fluoride emissions. Through this same contract, ADL recommended a complete procedure which looked best on the basis of their laboratory evaluations. This method or procedure is herein referred to as the Arthur D. Little or ADL method.

Subsequent to the completion of ADL's work, EPA contracted with Environmental Engineering, Inc., the predecessor of the reporting firm, to perform a field evaluation of the ADL method using various field sources of fluoride with the following objectives:

1. To perform a complete evaluation of a proposed EPA fluoride sampling method prepared under contract by Arthur D. Little, Inc.

2. To compare the performance of the above EPA method with a method currently being used by industries having fluoride emissions.

3. To develop a continuous fluoride monitor, measuring soluble fluorides, to be operated simultaneously with the evaluation test of items 1 and 2.

During the process of achieving these objectives, policy decisions in EPA resulted in the abandonment of the ADL method as the acceptable EPA method. This change affected both the sampling train and the analytical procedure. At the time of this shift, there was a corresponding shift in the evaluation project to reflect the new sampling train configuration and new analytical procedure herein identified as the C. E. Decker (Decker) method.

In view of these mid-stream shifts, the reader is subject to become confused when reviewing the seeming multiplicity of methods studied.

2.0 METHODS REVIEW

2.1 SAMPLING TRAINS

During the course of this project, three distinct sampling trains were used as illustrated in Figures 1, 2, and 3.

Figure 1 illustrates the train as recommended by ADL, which is essentially the system popularly identified as EPA method 5. Other details of this train are specified in Appendix A of this report, which consists of material reproduced from the ADL report to EPA.

Figure 2 illustrates the train currently recommended by EPA, used in conjunction with the Decker analytical procedure, to make up EPA method 13 as described in Appendix B.

Figure 3 illustrates the "Florida" train. This system is that specified by the State of Florida. It differs physically from the previous two primarily in that it has a stainless steel probe, no filter, and no ice bath requirement.

2.2 MEASUREMENT METHODS USED IN THIS STUDY

2.2.1 APPLICATIONS IN REGARD TO PROJECT ORIENTATION

The original project orientation in regard to measurements was to evaluate the Arthur D. Little Method by comparison with the Inter-Society Committee Method[32] for steam distillation from perchloric acid, using field and laboratory samples. This work is principally described in Section III, 1.0.

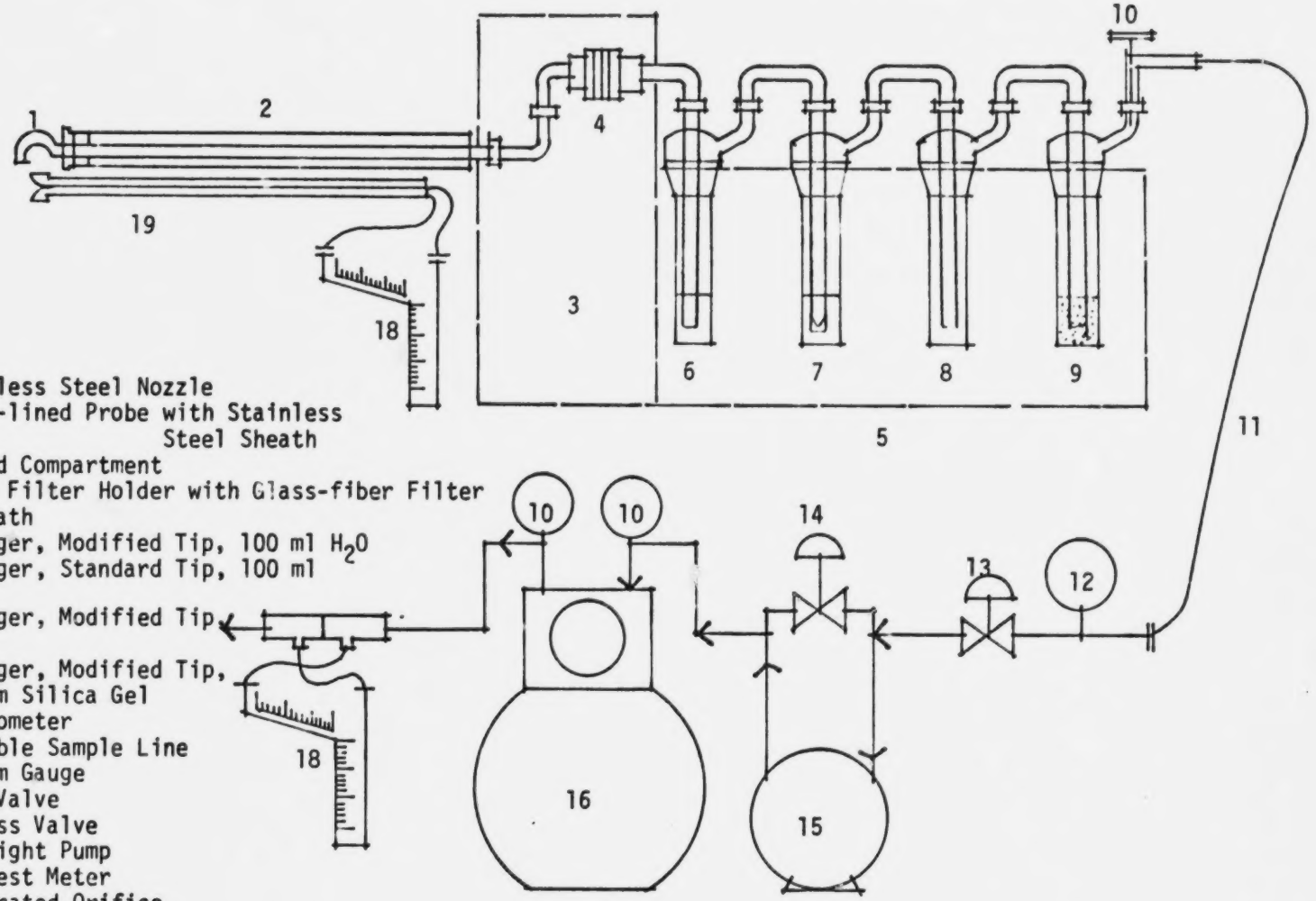
Subsequently, the work was reoriented towards primary evaluations of the Decker method and, later, the EPA method 13 (similar to the Decker method) to coincide with the new directions received from the EPA project officer. Although the measurement mode recommended for EPA 13 and Decker method was colorimetric, electrode measurements were done concurrently to the extent necessary to allow a valid comparison of the two measurement techniques under similar conditions.

2.2.2 DESCRIPTIVE COMPARISON OF METHODS

Table 1 contains data necessary to allow a general comparison among fluoride determination methods used in this study. The Appendixes contains copies of the methods evaluated.

2.2.2.1 Arthur D. Little Method

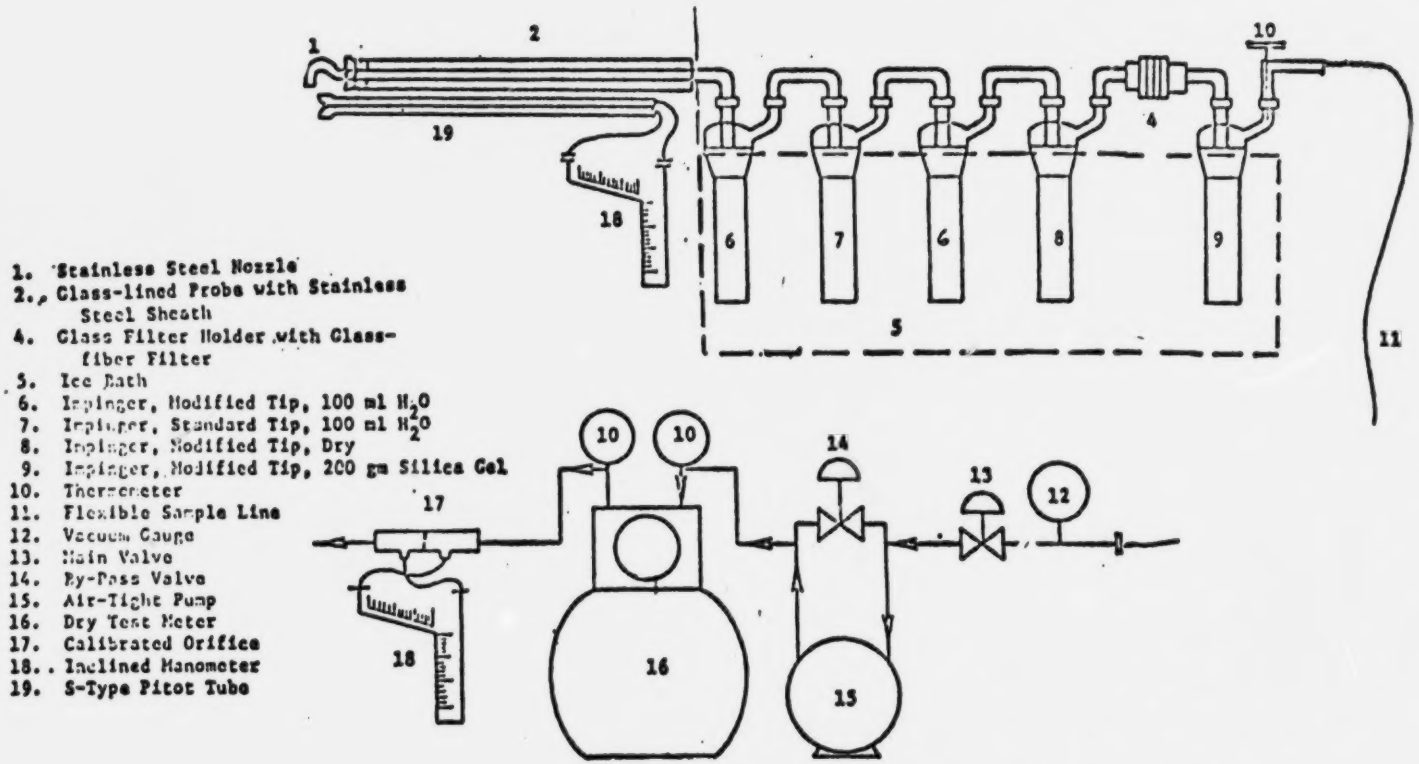
In general, the sample solution is treated by the following procedural sequence: The solution is buffered and fluoride concentration measured by electrode (measurement range: 0.02-2,000 µg/ml) to determine an aliquot volume size ($\leq$3000) which contains fluoride within the range of



1. Stainless Steel Nozzle
2. Glass-lined Probe with Stainless Steel Sheath
3. Heated Compartment
4. Glass Filter Holder with Glass-fiber Filter
5. Ice Bath
6. Impinger, Modified Tip, 100 ml H_2O
7. Impinger, Standard Tip, 100 ml H_2O
8. Impinger, Modified Tip Dry
9. Impinger, Modified Tip, 200 gm Silica Gel
10. Thermometer
11. Flexible Sample Line
12. Vacuum Gauge
13. Main Valve
14. By-Pass Valve
15. Air-Tight Pump
16. Dry Test Meter
17. Calibrated Orifice
18. Inclined Manometer
19. S-Type Pitot Tube

EPA Method 5 Particulate Sampling Train

FIGURE 1



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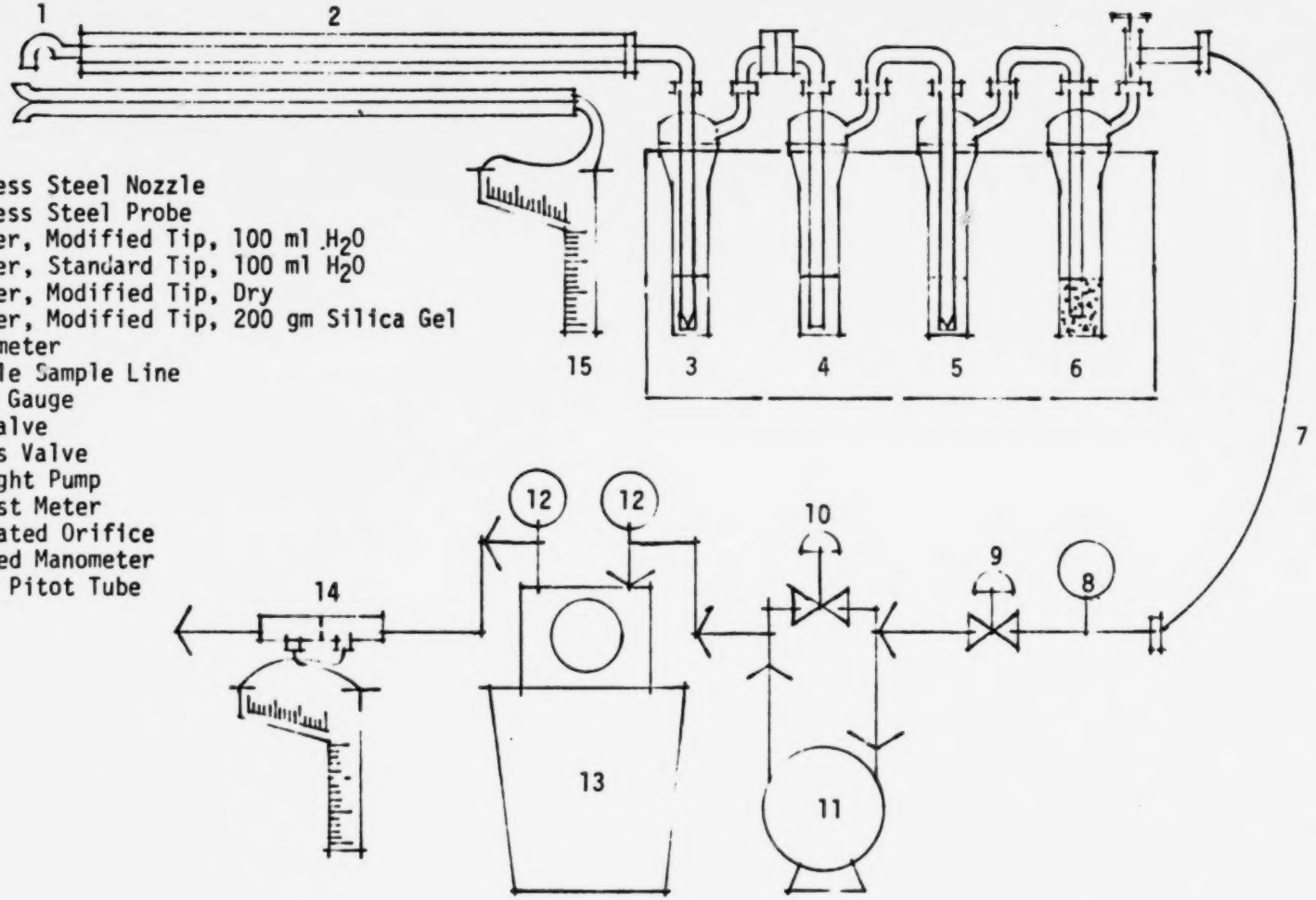
15. Air-Tight Pump
16. Dry Test Meter
17. Calibrated Orifice
18. Inclined Manometer
19. S-Type Pitot Tube

Proposed EPA Fluoride Sampling Train

Figure 2



1. Stainless Steel Nozzle
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12. Air-Tight Pump
13. Dry Test Meter
14. Calibrated Orifice
15. Inclined Manometer
16. S-Type Pitot Tube

Modified Floride Train

FIGURE 3

TABLE 1

A COMPARISON OF FLUORIDE DETERMINATION METHOD PARAMETERS

Method	Distillation			Measurement Mode	
	Type	Acid	Temperature	SPADNS Colorimetric	Electrode
A. D. Little	Direct	Sulfuric	210°C	-	Used
Intersociety[3] Committee, A	Steam	Perchloric	135 ± 2°C	Used	-
Intersociety[3] Committee, B	Steam	Sulfuric	165 ± 5°C	Used	-
C. E. Decker	Direct	Sulfuric	180°C	Used	-
EPA 13	Direct	Sulfuric	180°C	Used	-

0.1 to 0.9 mg. The aliquot volume is adjusted to 300 ml and distilled after addition to a 300 ml solution of sulfuric acid in a one-liter flask. Specific details of sample handling techniques are not provided here since they are not of primary importance in a comparison of methods. The final temperature of 210°C for distillation would insure complete recovery without contribution of a positive sulfate interference since the elctrode, in contrast to the SPADNS colorimetric method, is not so much affected by sulfate ion.

2.2.2.2 C. E. Decker and EPA 13 Methods

The C. E. Decker and EPA 13 methods essentially are equivalent and both are similar to the A. D. Little Method, except that the distillation temperature is lower (180°C) to minimize a positive interference of sulfate ion upon the SPADNS colorimetric measurement method (measurement range: 0 to 1.4 ppm fluoride).

2.2.2.3 The Intersociety Committee Methods

The Intersociety Methods (A and B) are equivalent except for acid type and distillation temperature. Perchloric acid is used if the sample contains no fluoride-complexing ions (such as Al^{+++}, Fe^{+++}, or Pb) which, in sufficient concentration, could retard recovery at 135°C, but less so at a higher temperature (sulfuric acid at 165°C). The distillation by steam is carried out in a smaller (250 ml) flask than that used in the A. D. Little Method and accommodates a sample volume of 50 to 75 ml with a fluoride content range of 100 mg down to a few micrograms.

3.0 LABORATORY ACTIVITIES

3.1 PRELIMINARY EXPERIMENTATION WITH THE ARTHUR D. LITTLE METHOD VERSUS INTERSOCIETY METHOD

3.1.1 DISTILLATION SYSTEMS CONSTRUCTION AND INITIAL TESTING

Two separate distillation racks were fitted to run six each of sulfuric and perchloric acid distillations simultaneously in order to compare the two methods.

During preliminary testing of the distillation systems, it was found necessary to order teflon sleeves for all glass joints in the sulfuric acid stills after several stopcock greases were tried unsuccessfully in an effort to prevent slow contamination by them in the distillates. This grease content would have been detrimental to the fluoride electrode by the resultant coating of the lanthanum sensing crystal with an impenetrable grease film. The 76 mm immersion thermometers lost their markings by action of the hot acids and replacement 280 mm immersion thermometers were ordered so that the markings would be outside the distillation head. Comparative calibration showed the two thermometers to be equivalent (within 0.05°C).

3.1.2 PRELIMINARY LABORATORY SAMPLE DETERMINATIONS WITH THE SULFURIC ACID/ELECTRODE COMBINATION (ADL METHOD)

3.1.2.1 Procedure

A calibration curve of log fluoride versus mv generated by an Orion Model 401 Fluoride-Specific Ion Meter was plotted on a 10 x 15-inch, five cycle semi-log graph paper over a fluoride range of 10^{-6} to 10^{-1} mol.

Six sulfuric acid distillation units were prepared for the following samples run simultaneously on stills #1 through #6: (1) blank, no fluoride added, (2) fusion with glass filter present (52.6µ mol of fluoride, as NaF), (3) fusion without filter present (52.6µ mol of fluoride, as NaF), (4) a phosphate plant scrubber sample (51.4µ mol of fluoride....as reported by a commercial analytical laboratory), (5) 153µ mol of fluoride, as NaF and (6) 7,900µ mol of fluoride, as NaF.

The acid-water ratio was adjusted in the stills and a predistillation blank run through each. The samples were run next, followed by two post-distillations. These data appear in Table 2.

3.1.2.2 Discussion of Results

Sample 1 (blank) decreased to 1.3µ mol of fluoride, which was an indication that the new system initially leached fluoride. This conclusion was also based upon second post-distillation levels of 1.3,

TABLE 2

RECOVERY OF FLUORIDE USING DIRECT DISTILLATION FROM SULFURIC ACID AT 210°C

Still No.	Sample	Fluoride added (μ mols)	Pre-Dist.	Sample Dist.	First Post-Dist.	First Post-Dist.	Sample Dist. %	Second Post-	% Rec.*
1	Blank	0.00	7.21	6.10	9.20			1.31	-
2	NaF fusion with glass filter	52.6	6.00	150	30.0	16.7		2.90	322
3	NaF fusion without glass filter	52.6	3.60	65.3	6.10	4.0		1.31	122
4	Phosphate plant scrubber	51.4	3.60	50.0	20.0	35.0		1.00	122
5	NaF	153	3.60	150	12.6	8.4		1.00	98.4
6	NaF	7,900	3.60	7,050	316	4.5		19.00	93.4

*Percent recovery for each sample was based upon subtraction of reagent blanks (μ mol of fluoride found in the pre-distillation from both sample distillation and first post-distillation, except for samples #2 and #6 in which the second post-distillation was added, minus 1.3 μ mol of fluoride (a typical background level found for second post-distillations in samples #1, 3, 4 and 5).

1.0, and 1.0 μ mol of fluoride for samples 3, 4, and 5, respectively, each of which had high pre-distillation levels.

Sample 2 percent recovery indicated either a lab error or fluoride in the glass filter. The fluoride level in second post-distillation was relatively high compared to that for samples 3, 4, and 5.

Sample 3, although at 122 percent recovery, indicated by its 6.1 μ mols first post-distillation that first post-distillations would likely be required to return to a normal background of about 1.3 μ mols.

Sample 4 indicated that first post-distillations would be necessary.

Sample 5 indicated that even at a fluoride level of 158 μ mols (three times that of Sample 3), a first post-distillation was sufficient to recover the sample.

Sample 6, with a fluoride concentration 50 times that of Sample 5, was largely accounted for in the sample distillation and first post-distillation, although a total recovery of only 93.4 percent was found. This high level of fluoride would not be distilled under normal analysis conditions and was used to test the system with a high fluoride concentration.

3.1.2.3 Conclusions

The lower concentrations of fluoride (51.4 to 52.6 μ mols) in this series were slightly above that (47.4 μ mols) recommended by Bellack in the Arthur D. Little, Inc. Final Report as being the maximum concentration for good recovery without a condenser rinse; so, it was apparent that some fluoride concentrations below 47.4 μ mols should be run to test the system for completeness of recovery in the Sample Distillation without a condenser rinse or post-distillation. However, in the interest of overall precision in the method from distillation through electrode measurement, concentrations higher than 47.4 μ mols of fluoride could be read in a fluoride concentration range of the fluoride electrode calibration curve, such as 10^{-4} to 10^{-3} mol, which has a faster and more precise electrode response than obtainable in the 10^{-6} to 10^{-4} mol range. Complete sample recovery without a post-distillation should, therefore, not overshadow the possible increase in measurement precision obtainable with higher fluoride concentrations in the distillation step for samples of sufficient concentration.

3.1.2.4 Comments

The Model 401 Orion Specific Ion Meter used in this experiment was found to be of very limited value in fluoride measurements over a concentration range of more than one molarity decade, because only one decade could be standardized at a time. Measurements on unknown

solutions required many new, time-consuming, narrow range standardizations or equally laborious dilution sequences to bring each into a prestandardized narrow range.

The ADL Method stated that a wide dynamic range calibration curve could be constructed over the range 10^{-2} to 10^{-6} mol with a digital readout meter. The alternate, direct readout meter procedure should have been designated as a poor one due to its time-prohibitive, narrow range (one decade) calibration limitation. A Model 801 Orion digital meter was ordered to alleviate this problem.

3.1.3 PRELIMINARY FIELD SAMPLE DETERMINATIONS WITH SULFURIC ACID/ELECTRODE AND SPADNS COMBINATIONS

3.1.3.1 Procedure

The set of field samples collected at a diammonium phosphate plant during December, 1972, was distilled by sulfuric acid at 210°C (A.D. Little Method) and then analyzed by the fluoride electrode (with the Model 801 Orion Meter) and Intersociety Committee SPADNS-ZIRCONIUM LAKE Method (using a Beckman UV Spectrophotometer). This was a trial effort and data was generated to the extent necessary to indicate procedural adequacy for more involved future analyses. A continuous fluoride monitor was run simultaneously in the same sample ports as were the two Florida trains. Actual fluoride concentrations in the stack gases and a comparison of electrode measurement results with continuous monitor electrode results is reported in Sections IV and V of this report.

3.1.3.2 Discussion of Results and Conclusions

No statistics on analytical precision, accuracy, etc., were determined for these preliminary samples. The results as shown in Table 3 were useful however in that the combined sampling and analytical precision was reasonably good considering the apparent low fluoride concentration at the DAP outlet and small number of samples involved.

The two comparisions of SPADNS to electrode results of 68 percent and 72 percent was not in agreement with the conslusion generally held by ADL that sulfate in sulfuric acid distillates was a positive interference in SPADNS measurements. This prompted careful attention to calibration procedures for both methods of measurement.

3.1.4 PRELIMINARY LABORATORY SAMPLE DETERMINATION WITH PERCHLORIC ACID/SPADNS COMBINATION (INTERSOCIETY COMMITTEE METHOD)

3.1.4.1 Procedure

A series of six known sodium fluoride standards was run simultaneously on a six-station distillation system to determine recovery efficiency.

TABLE 3

PRELIMINARY WATER SOLUBLE FLUORIDES ANALYSIS-TRIPLE SUPER PHOSPHATE PLANT

Sampling Train	Sampling Date	Train Filter mg F			Impinger and Probe Wash, mg F			Total mg F	
		ELEC	SPADNS	SPADNS/ELEC %	ELEC	SPADNS	SPADNS/ELEC %	*ELEC	SPADNS
EPA Run #1	12/20/72	0.463			2.127			2.590	
FLA Run #1	12/20/72	---			2.476			2.476	
EPA Run #2	12/21/72	3.998	2.719	68.0	1.329	0.962	72.4	5.327	3.681
FLA Run #2	12/21/72	---			4.123			4.123	

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3.1.4.2 Discussion of Results and Conclusions

With reference to Table 4, a point of significance bearing upon the percent recovery of still 6 was that some condensate was lost in the vapor state at the beginning of the run due to the system's condenser-water flow decreasing to a very low rate by virtue of a water pressure drop after initial adjustment of the flow rate. This occurred over a period of about 30 seconds and the effect upon the other samples is considered to be negligible since the condenser water was hottest at the end-most condenser, 6 and very little condensate vapor was observed in flask 5.

Statistical analysis of the adjusted final percent recovery for samples 1-5 yields a mean of 98.9 percent, with standard deviation, 5.21 percent defining a 95 percent confidence interval of 10.42 percent. Ten percent, plus or minus, of the amount of fluoride in the sample to be distilled is considered an acceptable deviation by the Intersociety Committee, although recoveries of mean, approximately 99 percent, and standard deviation, 2.5 percent have been reported under favorable circumstances of sample composition and fluoride range. This accuracy and precision would have been exceeded had sample 3 been excluded.

The negative values for predistillation are valid as determined by an experiment in which 10-ml volumes of tap and distilled water were evaporated at 80°C and measured for fluoride. The tap water contained approximately 0.94 ppm and distilled, approximately 0.05 ppm or 1.25 µg/25 ml. The steam generators were filled with this distilled water. The resulting second distillation (from the steam generator into the sample flask) would decrease the fluoride to possibly 50 percent of the original 0.05 ppm to result in negative backgrounds of this concentration magnitude when compared to the standard calibration curve prepared by measurements upon single-distilled water fluoride standards.

Since the steam generators in this experiment had been used several times previously with varying total volumes of distilled water and were not rinsed out prior to the experiment, the resulting predistillation background fluoride concentrations were of higher variability than would be expected in the case of generator rinse-outs preceding each experiment. Therefore, steam generators should be rinsed out each time to avoid steam generator fluoride build-up by this means and to facilitate the development of consistent predistillation backgrounds. If this is done, only one or two determinations would be necessary as a check on conformity to a system predistillation fluoride level (predetermined as a mean with 95 percent confidence range over a system-set of six predistillations).

An important conclusion by comparison of corrected percent recovered, adjusted percent recovered, and adjusted final percent recovered is that pre- and post-distillation fluoride levels do not significantly change the corrected percent recovered values and would be an unnecessary analysis step in the case of pure NaF up to at leat 17.5 mg fluoride.

TABLE 4

RECOVERY OF SODIUM FLUORIDE DISTILLED BY INTERSOCIETY METHOD - PERCHLORIC ACID

Flask and Sample	Known mg F^-	(1) Distillate Aliquot (ml)	DU Cell #	Cell Corr.	(2) Expec. µg/Aliq.	Absorb. Read (µu)	Corr. Abs. (mµ)	Corr. µg/Aliq.	Corr. % Rec.	(3) Corr. Pre-Dist. µg/Aliq.	(4) Adj. µg/Aliq.	Adj. % Rec.	(3) Corr. Post-Dist. µg/Aliq.	(5) Adj. Fin. µg/Aliq.	Adj. Fin. % Rec.
1	2.51	3.00	4	+0.012	30.12	0.224	0.236	30.000	99.60	-0.0375	30.038	99.7	-0.0375	30.038	99.7
2	5.01	1.50	2	+0.016	30.06	0.222	0.238	29.625	98.55	-0.0375	29.663	98.7	0.2160	29.879	99.4
3	7.54	1.00	4	+0.012	30.16	0.2[illegible]5	0.257	27.125	89.94	-0.0625	27.188	90.2	0.0625	27.251	90.4
4	10.00	0.50	2	+0.016	20.00	0.294	0.310	20.000	100.00	-0.0063	20.006	100.0	0.0345	20.041	100.2
5	12.50	0.50	4	+0.012	25.00	0.252	0.264	26.175	104.70	-0.0031	26.178	104.7	0.0050	26.183	104.7
6	17.50	0.50	2	+0.016	35.00	0.219	0.231	30.625	87.50	0.0000	30.625	87.50	0.0845	30.710	87.7

(1) Pipets used for aliquots were 0.50, 1.00, and 3.00 ml with 15 second drainage periods.

(2) Expected µg/Aliq. is calculated by: Exp. µg/Aliq. = $\frac{\text{Aliquot (ml) (known F, µg)}}{250 \text{ ml}}$.

(3) Corrected Pre-or Post-Distillation as µg/Aliq. was determined in the same fashion as was Corr. µg/Aliq. for the sample, except aliquot size was 20 ml which required conversion by proportion to represent the corresponding Distillate Aliquot.

(4) Adjusted µg/Aliq. is Corr. µg/Aliq. after further correction with Corr. Pre-Distillation, by, Adj. µg = Corr. µg/Aliq.—Corr. Pre-Distillation.

(5) Adjusted Final µg/Aliq. is Corr. µg/Aliq. after further correction with Corr. Pre- and Post-Distillation values, by, Adj. Fin., µg = Corr. µg/Aliq.—[Corr. Pre-D. - (Corr. Post-D. - Corr. Pre-D.)].

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In the case of analysis of a particular industry's emissions with known interferences that would tend to retain fluoride in the distillation step (such as Al +++), distillation should first be done by sulfuric acid as specified by the Intersociety Committee Method.

3.2 EXPERIMENTATION USING THE SULFURIC ACID/SPADNS TYPE METHOD WITH SOME ELECTRODE MEASUREMENT COMPARISONS

3.2.1 FLUORIDE RECOVERIES AT VARIOUS FINAL TEMPERATURE BY DIRECT SULFURIC ACID DISTILLATION (C.E. DECKER METHOD)

3.2.1.1 Procedure

This experiment was designed to compare recovery of fluoride distilled at 180, 195, and 210°C by the SPADNS vs electrode measurement modes and to confirm the upper fluoride charging limit for distillation as specified by the C. E. Decker Method.

The C. E. Decker Method indicated that to insure complete recovery, aliquots of no more than 0.9 mg fluoride should be distilled. Samples containing 1.0 mg fluoride (as NaF) were distilled to test the limit. The final distillation temperature effect upon recovery was also of interest in view of the fact that 180°C was used in the Decker Method and 210°C in the A. D. Little Method.

After initial acid/water adjustment, the distillation flask must be cooled before addition of the sample. Sixty degrees, as recommended by Little, was used instead of 120°C, as recommended by Decker, since the flask at 60°C could be handled with greater operator safety. It was thought desirable to include a test for fluoride loss due to the flask being charged at 60°C versus charging at room temperature.

The effect of sulfate was to be examined by measurement of a post acid-adjustment distillation (predistillation).

Sensitivities for each method at a particular temperature were defined as a response equal to two times the predistillation measurement.

A post-distillation was included to insure complete recovery, and for the purpose of examining the effect of final distillation temperature upon the percent of total fluoride recovered.

3.2.1.2 Discussion of Results and Conclusions

With reference to Table 5, the percent of total recovery in the post-distillate by SPADNS and electrode at 180°C was about 16 percent for both, 8.5 to 9.5 percent at 195°C and about 4 percent at 210°C (disregarding the erroneous 12 percent for one electrode measurement). Therefore, at 180°C, some quantity less than 1.0 mg fluoride would be maximum for complete recovery in one distillation. Even at 210°C, only 96 percent recovery could be expected. The first five samples were evaluated statistically, wherein it was found that the total recoveries for the SPADNS measurement mode were determined with a relative error of 2.64 percent and relative precision of 2.72 percent which compared favorably with results by Standard Methods.[2] The corresponding values for the electrode were 6.74 and 2.6 percent respectively. The higher electrode value for relative error amounted to a

TABLE 5

SODIUM FLUORIDE RECOVERIES AT VARIOUS FINAL TEMPERATURES BY DIRECT SULFURIC ACID DISTILLATION

Sample Addition Temperature	Final Temperature	Predistillation[a,b]		Distillation[a]		Postdistillation[a,c]		Recoveries[a]			
		SPADNS mg	ELEC mg	SPADNS mg	ELEC mg	SPADNS mg	ELEC mg	SPADNS Total mg	SPADNS Post-D Total (%)	ELEC Total mg	ELEC Post-D Total (%)
RT	180°C	0.019	0.038	0.819	0.872	0.162	0.174	0.981	16.5	1.046	16.6
60°C	180	0.019	0.035	0.819	0.875	0.150	0.173	0.969	15.5	1.048	16.5
RT	195	0.038	0.042	0.837	0.958	0.093	0.092	0.930	10.0	1.050	8.8
60°	195	0.031	0.031	0.907	1.019	0.088	0.089	0.995	8.8	1.108	8.0
RT	210	0.069	0.044	0.931	1.046	0.062	0.039	0.993	6.2	1.085	3.6
60°	210	0.075	0.032	0.950	1.058	0.013	0.145	0.963	1.3	1.203	12.0
Averages			0.037					.974		1.070[e]	

[a]Corrected for background as determined by predistillation fluoride level for each sample.

[b]Predistillation was the first distillation after the acid-water ratio adjustment.

[c]Postdistillation was the distillation that followed the sample distillation.

[d&e]Averages for the first five values only.

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bias of a positive 9.4 percent compared to SPADNS. The error was thought to be due to an erroneous segment of the electrode curve since the values were consistently higher than SPADNS in the corrected main distillation but not in the corrected post-distillation.

No significant difference in total recovery was found for the first five samples charged at flask temperatures of room temperature versus 60°C. This was tested since it was thought that some fluoride might be driven off from a 60°C flask while the flask was being reassembled into the still after sample addition.

The effect of sulfate ion upon SPADNS was reflected in the predistillation where the average magnitudes at 180°, 195° and 210°C were 0.019 mg, 0.035 mg and 0.072 mg, respectively. These magnitudes are convertible to method sensitivities when multiplied by a factor of two. There was no apparent distillation temperature effect upon predistillation values for the electrode over the distillation range of 180 to 210°C, where the average was found to be 0.037 mg., or a sensitivity of 0.074 mg.

There were no differences apparent for SPADNS total recoveries at 180°C versus 195° or 210°C. From inspection of the first five samples by the electrode it appeared that possibly a 3 or 4 percent total recovery increase was involved between 180°C and 210°C values, but the high variability of the last three values precluded a valid test of significance. However, in the C. E. Decker Method, where no background was determined for subtraction and no post-distillation performed, the recovery of 1.0 mg samples (assuming complete recovery) would be increased by the average electrode background percentage equivalent of 3.7 percent or the corresponding averages by SPADNS of 1.9, 3.5 and 7.2 percent at 180°C, 195°C and 210°C respectively. The above increases would be doubled in the case of 0.5 mg samples in a distillation performed with no background corrections.

Decker reported $\pm$ 4 percent as the error of his SPADNS analytical method. According to the results of this experiment there would be an experimental bias of plus 4 percent upon the recommended optimum sample size of 0.5 mg by virtue of background and not including experimental error. Positive background bias and negative experimental error due to incomplete actual recovery could cancel to various extents for various sample sizes near 0.5 $\pm$ 0.2 mg to result in an error of analytical method within the Decker reported range of $\pm$ 4 percent.

3.2.2 RELATIVE ERROR AND PRECISION FOR DETERMINATION OF 500 µg OF FLUORIDE BY SULFURIC ACID DISTILLATION OF 180°C, USING SPADNS COLORIMETRIC MEASUREMENT MODES AND ORION FLUORIDE ELECTRODE

3.2.2.1 Purpose and Procedure

The purpose of this experiment was to test the present EPA fluoride determination method (C. E. Decker) for relative error and precision using pure NaF solutions.

The procedure was designed to compare two variations in addition to the explicit EPA method. The EPA method specified that 0.5 to 0.9 mg of fluoride could be distilled without a post-distillation and with 0.5 mg designated as an optimum; it was designated as Method I. Method II was designated to include a post-distillation which was measured independently of the first distillate. In Method III, the post-distillation distillate was combined with an equal volume of the first distillate to allow a single measurement on the resulting solution.

Orion Fluoride Standard (solution #94-09-07, 100 ± 0.5 ppm) was used to prepare five 500 µg fluoride solutions for direct measurement with no previous distillation and five for distillation prior to measurement.

3.2.2.2 Discussion of Results and Conclusions

3.2.2.2.1 SPADNS-Zirconium Lake Measurement Mode

Except for Method I (see Table 6), relative error and precision compared favorably with those reported by Standard Methods[2] in which a synthetic unknown sample containing 830 µg/l was analyzed by 53 laboratories. Distillation with no post-distillation (Method I) failed to yield a complete recovery. The 830 µg/l sample referred to by Standard Methods[2] allowed a maximum of only 249 µg to be distilled in a 300 ml distillation charge volume. The fact that this study was done with twice this amount could possibly account for the difference in recovery.

Method III was found to be the preferred method in that it allowed complete recovery with a single measurement.

3.2.2.2.2 Electrode Measurement Mode

Except for the non-distilled NaF measurement bias as indicated by a high relative error (over-recovery in this case), the electrode statistics were superior to those of the colorimetric method.

3.2.3 SUMMARY OF EXPERIMENTS CONCERNING RELATIVE ERROR AND PRECISION FOR DETERMINATION OF 0.500 mg DISTILLED FLUORIDE: BY SULFURIC ACID DISTILLATION TO 180°C, USING SPADNS COLORIMETRIC AND ORION FLUORIDE ELECTRODE MEASUREMENT MODES

3.2.3.1 Procedure

The results were derived by the procedure of Section 3.2.2 above, and include distillation data of Section 3.2.2 under "Experiment #1" in Table 7.

3.2.3.2 Discussion of Results

It was apparent by comparisons of results of individual experiments in Table 7 that the Electrode was the better measuring mode since in the

TABLE 6

STATISTICS SUMMARY FOR 0.500 mg NONDISTILLED AND DISTILLED FLUORIDE DETERMINATIONS

Measurement Mode	Statistic	Nondistilled NaF		Distilled NaF			
				Method			
		Found By Experiment	"Standard Methods"*	I	II	III	"Standard Methods" Method I
SPADNS	Mean, mg	0.493	-	0.397	0.504	0.509	-
	Relative error	1.4%	1.2%	20.6%	0.8%	1.8%	2.4%
	Relative Std. Deviation	1.7%	8.0%	3.7%	4.3%	4.9%	11.0%
ELECTRODE	Mean, mg	0.529	-			0.505	-
	Relative error	5.7	0.7			1.0	-
	Relative Std. Deviation	1.7	3.6			1.8	-

Method I - C. E. Decker method (EPA) as written.

Method II - C. E. Decker method (EPA) with post distillation, each measured independently.

Method III - C. E. Decker method (EPA) with post distillation, two distillates combined for single measurement.

*See 2.2.2.1 and 2.2.2.2.

TABLE 7

FLUORIDE RECOVERY USING 0.5 mg STANDARD SAMPLES WITH THREE DISTILLATION METHODS AND TWO MEASUREMENT MODES

Measurement Mode	Statistic	Experiment #1 Method			Experiment #2 Method			Experiment #3 Method			Experiment #4 Method			Standard Methods Method		
		I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
SPADNS	Mean, mg	0.397	0.504	0.509	-	-	0.472	0.449	0.538	0.542	0.426	0.553	.527	None	None	None
	Relative Error	20.6	0.8	1.8	-	-	5.7	10.1	7.6	8.4	14.7	10.5	5.4	2.4	None	None
	Relative Std. Deviation	3.7	4.3	4.9	-	-	2.5	6.4	4.7	1.9	2.9	4.7	2.4	11.0	None	None
ELECTRODE	Mean, mg	-	-	0.505	-	-	-	0.460	0.553	-	0.421	0.522	-	None	None	None
	Relative Error	-	-	1.0	-	-	-	8.0	10.7	-	15.8	4.4	-	None	None	None
	Relative Std. Deviation	-	-	1.8	-	-	-	3.0	3.2	-	3.8	2.0	-	None	None	None

Method I - C. E. Decker method (EPA) as written

Method II - C. E. Decker method (EPA) with post distillation, each measured independently

Method III - C. E. Decker method (EPA) with post distillation, two distillates combined for single measurement.

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cases where its relative standard deviation was lower than that of SPADNS, its corresponding relative error was also lower. Average relative errors and average relative standard deviations among electrode mode results for all methods of the four experiments were calculated and found to be 8.0 and 2.8 percent respectively. These averages were compared to corresponding averages of 8.9 and 4.7 percent found for the SPADNS mode among only those experiment methods for which the electrode and SPADNS modes were jointly used. Expressed as a percentage comparison of electrode averages to SPADNS averages, the electrode relative error and relative standard deviation was found to be 90 and 60 percent, respectively, of the respective corresponding statistics for SPADNS. The relative error of 2.4 percent reported by Standard Methods[2] for Method I (Table 7) was considerably lower than those obtained in these SPADNS and electrode measurements, but the relative standard deviation of 11.0 percent was considerably higher than those obtained herein and may be interpreted as not being as valid an estimate as that determined herein of the SPADNS relative error in the Method I classification.

3.2.4 ISOLATION OF FLUORIDE RESIDUE LOCATION IN FLUORIDE STILL AFTER DISTILLATION

3.2.4.1 Introduction

A preceding (3.2.2) experiment indicated that for five samples an average of 20.6 percent fluoride remained in the still after the first distillation and a post-distillation was required to obtain satisfactory recovery on the samples. The experimental results obtained by measurement upon a solution containing equal aliquots of the initial distillate and a post distillation, 1.8 percent relative error and 4.9 percent relative standard deviation, compared favorably to those by Standard Methods[2] for an 830 µg/l sample; 2.4 and 11.0 percent respectively. However, the distillation procedure used for Standard Methods[2] did not include a post distillation.

3.2.4.2 Purpose and Procedure

The purpose of this experiment was to determine the cause of incomplete fluoride recovery in an initial distillation only (no post distillation included).

The method used was the following: After distillation of 0.5 mg fluoride, the still was allowed to cool to below 60°C and then the condenser, connecting arm, and still head were each separately rinsed inside with 50 ml distilled water to test for the location of the residue. The still was then reassembled, recharged with water, and a post distillate collected at 180°C. This procedure was then repeated (Run II) except that the used acid remaining from the initial distillation was siphoned out, replaced with fresh acid solution (previously acid-adjusted and blank-distilled), and swirled to wet the entire flask surface. The post distillate was then collected as before. Run III was

the same as Run II, except that preceding the post distillation, the flask was insulated on the above heater outside surfaces, and the new acid was added by pipet to the center of the flasks without subsequent swirling.

3.2.4.3 Discussion of Results

Replacement of the used acid in Run II with new, separately prepared, acid-adjusted solution did not decrease the post-distillate fluoride recovery when compared to Run I. Since fluorides recovered in the head, arm, and condenser for both runs I and II were very low, the major portion was isolated in the flask to the above-acid-level wall surface. The lower post-distillate recovery in Runn III was probably due to the fact that the newly introduced replacement acid was not swirled to remove fluorides adhering to the flask wall. Total recovery in Run III was below 0.50 mg for likely the same reason.

3.2.4.4 Conclusions

The fluoride remaining on the distillation flask wall was probably due to the relatively large surface area over which the distillate fluorides had to be distilled with a correspondingly low distillation efficiency at that point. Visual inspection of the distillation flask during distillation also supported the above statement, in that the reflux solution was composed of small droplets running down the flask surface in a pattern which was inefficient in covering the entire surface to insure release of all nonvolatile fluorosilicate intermediates of the gas, hexafluosilicic acid. The irregular nature of this reflux pattern could also account for the wide range of relative errors (10, 15, and 21 percent) for fluoride values summarized in Table 7 of 3.2.3 for Method I (no post distillate included).

3.2.5 FLUORIDES DETERMINATION BY STEAM DISTILLATION FROM SULFURIC ACID AND MEASUREMENT BY ORION FLUORIDE ELECTRODE OR SPADNS-ZIRCONIUM LAKE MODES

3.2.5.1 Purpose and Procedure

The purpose of this experiment was to test a fluoride determination method which would require no post distillation and which would retain sulfuric acid as the distillation medium.

The Willard-Winter Distillation Method by sulfuric acid was used, as per the Intersociety Committee's, "Methods of Air Sampling and Analysis, 1973," except that approximately 350-ml distillates were diluted to 500 ml for measurement.

Five samples containing 0.5 mg fluoride (NaF) each were distilled and measured by the SPADNS and electrode modes.

TABLE 8

DISTRIBUTION OF RESIDUAL FLUORIDE AMONG STILL COMPONENTS

Analysis Location	Run I, mg F	Run II, mg F	Run III, mg F
Distillate	0.416	0.374	0.422
Post Distillate	0.111	0.112	0.061
Condenser (Rinse)	0.004	0.005	--
Connecting Arm (Rinse)	0.003	0.004	--
Head (Rinse)	0.007	0.008	--
TOTAL	0.541	0.503	0.483

3.2.5.2 Discussion of Results and Conclusions

The electrode measurement mode was the better of the two (Table 9). SPADNS values were higher, probably due to positive sulfate interference.

The Willard-Winter Distillation Method was found to be better than one that required direct distillation from a one-liter flask, due to the necessity of only one distillation per sample and the low relative standard error (2.2 percent) and relative standard deviation (1.3 percent). The relative error would probably be even lower had quantities greater than 0.5 mg been distilled. In the broad fluoride range (0 to 100 mg) possible for distillation, quantities greater than 0.5 mg would be distilled more often than not, which would further insure low relative error results.

The distillation flasks can be continuously steam distilled between runs, with a large capacity steam generator, to insure a low fluoride background.

The small flask size (250 ml) facilitated continuous flask wall washing during distillation by vigorous bubbling of the contents by the incoming steam. The lack of this type flask wall purging probably allowed incomplete recovery in the direct distillation from a one-liter flask, as previously explained in 3.2.4 above.

According to the Intersociety Committee[3], the Willard-Winter distillation can accommodate quantities of fluoride ranging from 100 mg down to a few micrograms. Therefore, pretesting by electrode of a solution to be distilled could be done more rapidly and with less concern about overloading the still due to inaccuracies caused by electrode interferences in an undistilled and concentrated solution.

Relative error accrued in the steam distillation would be considerably lower than that for the direct distillation since fluoride quantities higher than the 0.5 mg optimum direct distillation quantity would more often be distilled.

This method (steam/sulfuric acid/electrode) was not as thoroughly evaluated as some other methods, so conclusions as to its preference over the other methods are tentative.

Ideally, a concentrated solution with interferences could be determined by electrode only, without prior distillation, by dilution of an aliquot to a low fluoride concentration in which the interferences would be dilute enough to render them cancelled as interferences.

3.2.6 ELECTRODE CALIBRATION MEASUREMENTS AS A FUNCTION OF TIME AT LOW SODIUM FLUORIDE CONCENTRATIONS

3.2.6.1 Purpose and Procedure

The purpose of this experiment was to determine relative electrode drift rates at low fluoride concentrations (10^{-5} and 10^{-6} mol) to aid in the

TABLE 9

MEASUREMENT STATISTICS FOR STEAM DISTILLED

FLUORIDES-SPADNS VERSUS ELECTRODE MEASUREMENT MODES

Measurement Mode	Mean[a]	Relative Standard Error	Relative Standard Deviation
Electrode	0.511 mg	2.16%	1.28%
SPADNS	0.527 mg	5.38%	1.03%

a. No background corrections applied.

development of a high-precision calibration procedure. The two fluoride concentrations were analyzed by taking successive readings on each at five minute intervals (Figure 4). The A. D. Little Method for electrode measurements was used throughout the analysis.

The cumulative effect of previous solution measurements at two different fluoride concentrations upon the current solution concentration measurements was tested as to its effect upon electrode drift. A series of three 0.05 ppm solution measurements were taken with 0.0125 ppm and 0.10 ppm solutions measured between the three successive 0.05 ppm solution measurements to determine their effect upon drift rate as noted between a five and a ten minute measurement taken sequentially on the same solution.

3.2.6.2 Results and Discussion

Dotted lines extrapolated back in time denoted slopes of the constant drift rate attained at time point A on both curves (Figure 4). Initial deviation from the constant drift rate line was approximately halved with each additional five minute interval to result in constant drift rates at 20.0 and 33.8 minutes for 10^{-5} mol (0.19 ppm) and 10^{-6} mol (0.019 ppm), respectively. The constant drift rate slopes for 10^{-5} and 10^{-6} mol were -38.1 and +25.3, respectively. The dotted lines were taken to be the true value at any designated time and errors defined as deviation from it at the ten-minute level were found to be 0.0038 ppm and 0.0047 ppm for 10^{-5} and 10^{-6} mol, respectively, when compared to a separate, smoothed, ten-minute calibration curve. The respective calculated relative errors were 2.0 and 24.7 percent.

The fact that the slopes of the two solutions studied were in opposite directions prompted a question as to whether previous measurement history ("measurement history" of the electrode was defined as the fluoride concentration or concentration matrix measured just prior to the in-progress measurement) of the electrode might determine magnitudes of deviation of a ten-minute measurement reading from a previously constructed ten-minute calibration curve. Three series-sets were analyzed to test for a "measurement history effect." Figure 5 shows the effect of series 1 measurements made in the noted sequence, 1-5. Magnitude and direction of slope are shown by a line drawn from the five-minute reading to the ten-minute reading for each solution concentration. Prior to measurement 1 on the 0.05 ppm solution, the electrode had been immersed overnight in a 0 ppm fluoride solution (routine procedure). The vertical lines denote the boundaries of measurements made at ten minutes for the 0.05 ppm solutions. Measurement series 2 and 3 (Figures 6 and 7) show the result of the same measurement sequence as in Figure 5, except that 0 ppm solution readings were developed for five minutes between each series measurement. Series 2 and 3 were tests of the effect of electrode normalization (0 ppm measurements preceding each measurement) upon history effect in regard to a 0.05 ppm solution concentration. The second series (Figure 6) had a measurement variation range of 1.4 mv compared to a 2.8 mv variation without 0 ppm measurements between individual series measurements in the first series (Figure 5). However, results in series 3 (Figure 7) had a measurement variation

FIGURE 4
MODEL 301 ORION METER READINGS AS A FUNCTION OF TIME

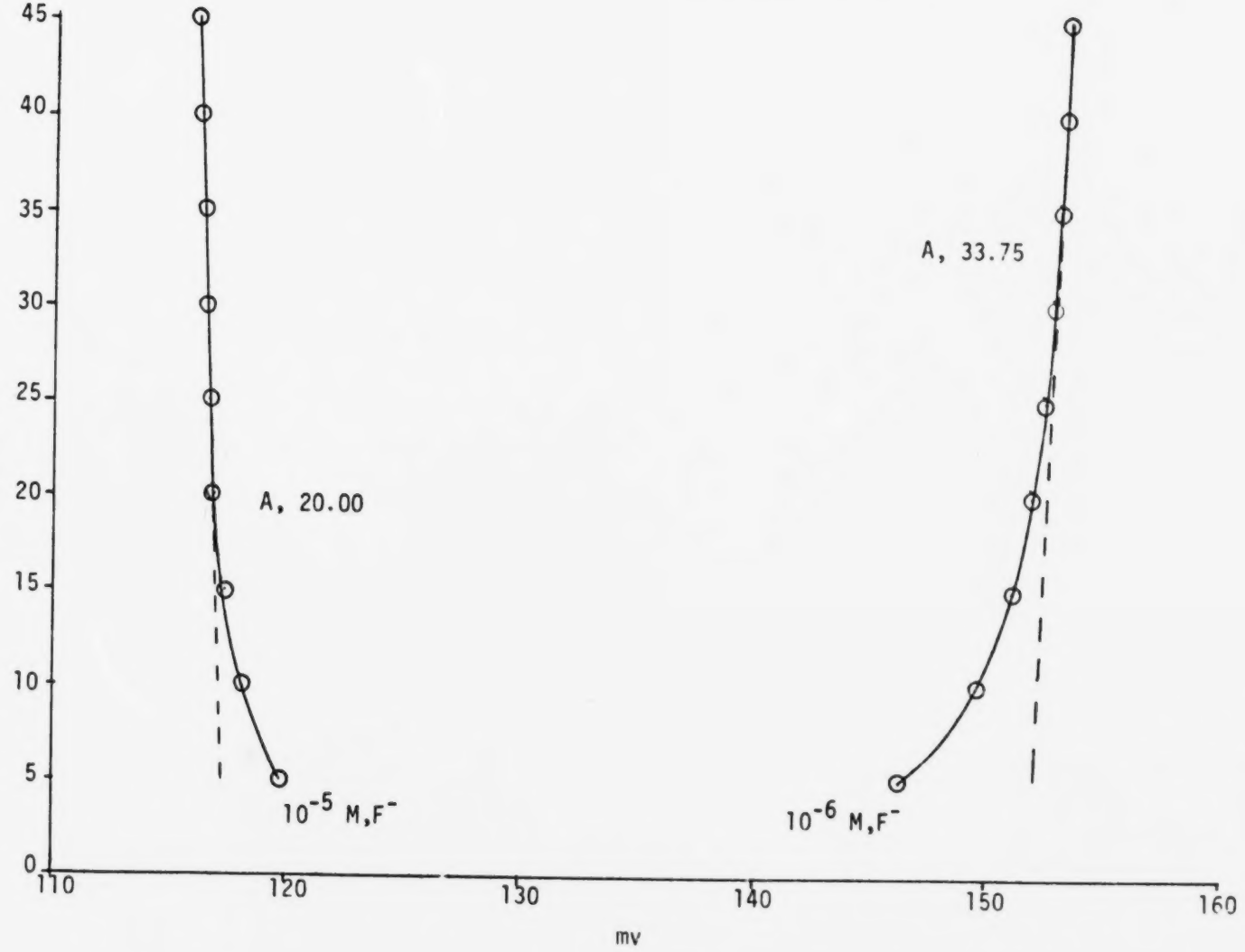
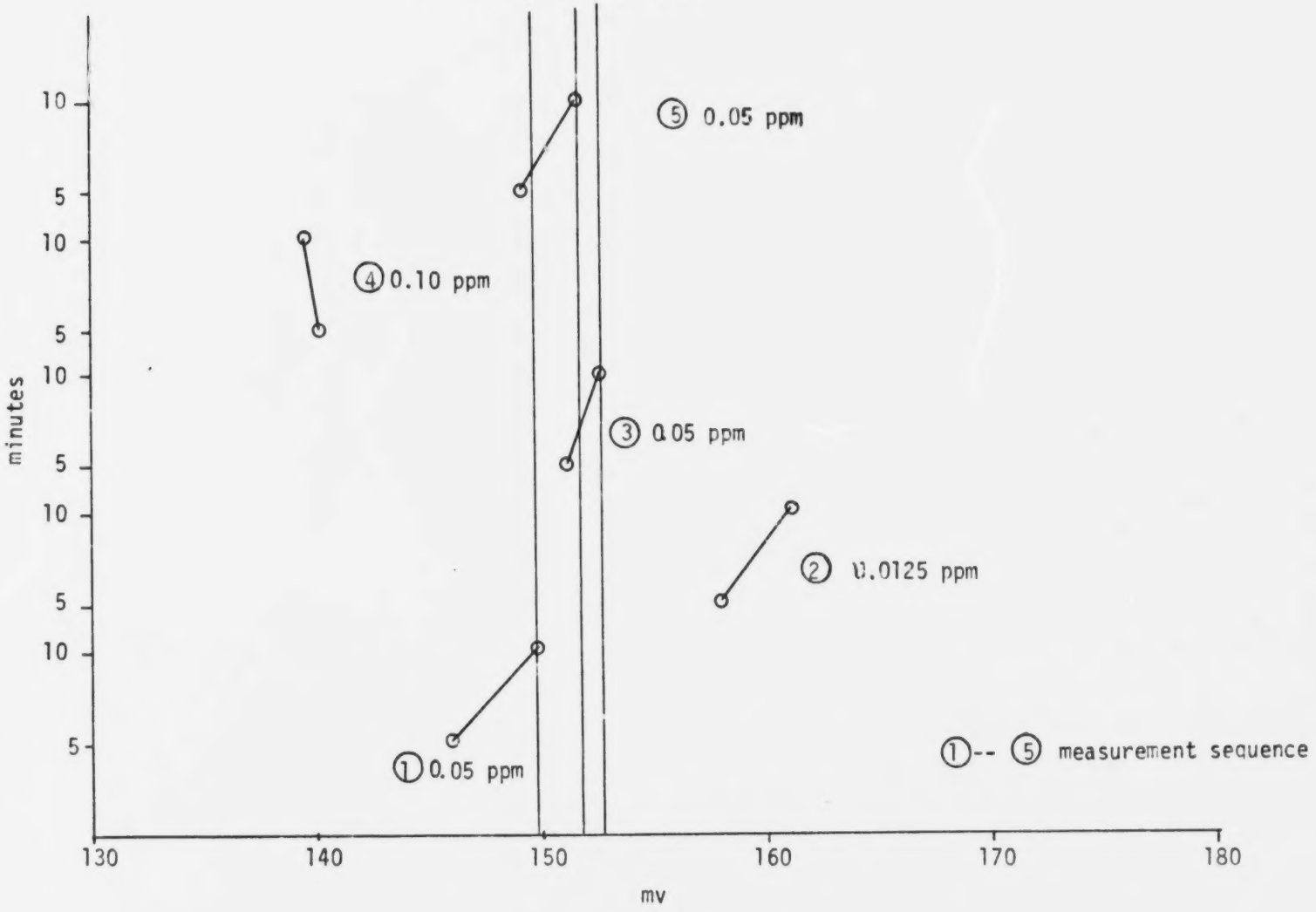


FIGURE 5

April 23, 1973

EFFECT OF ELECTRODE MEASUREMENT HISTORY UPON RESPONSE
SERIES 1



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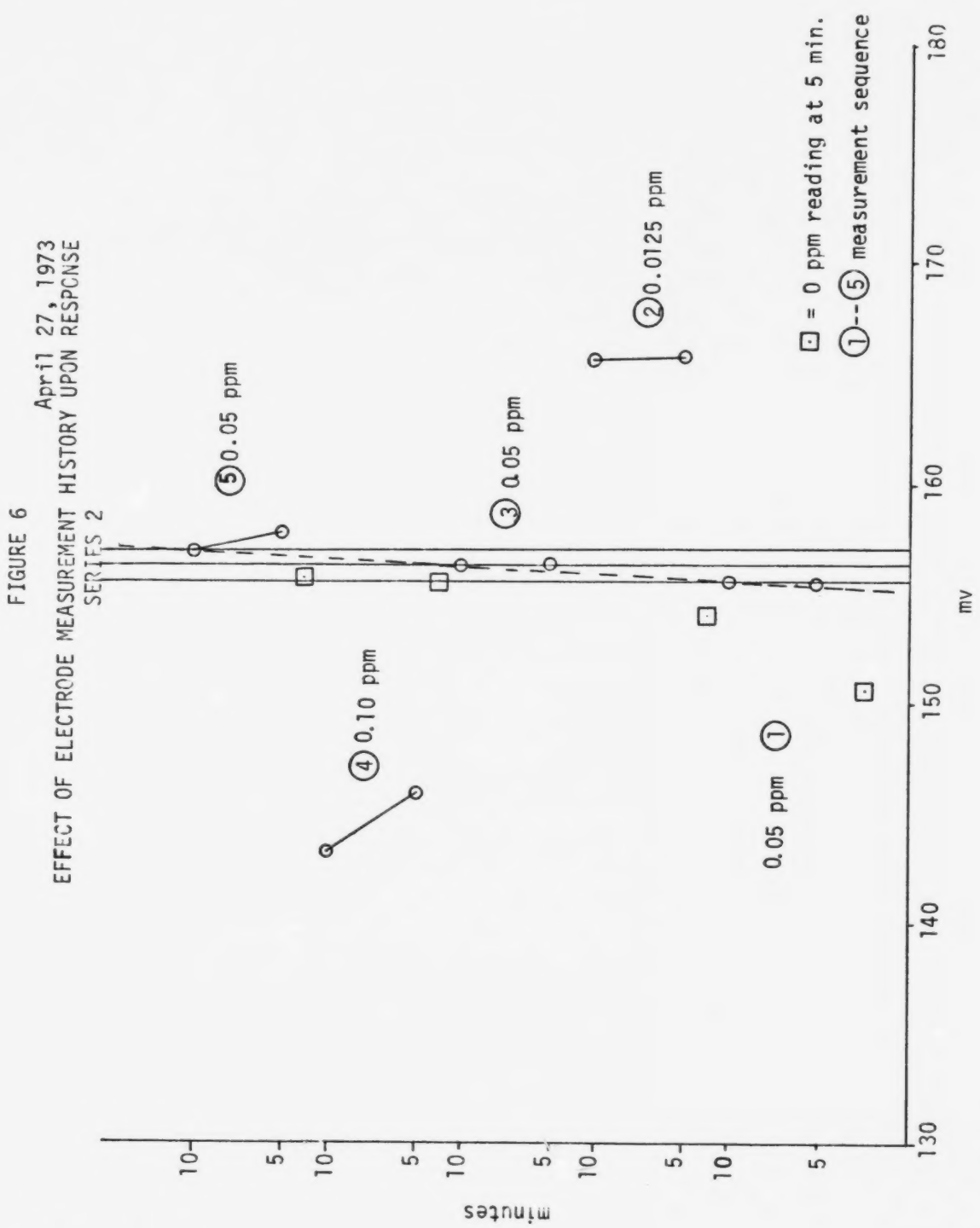
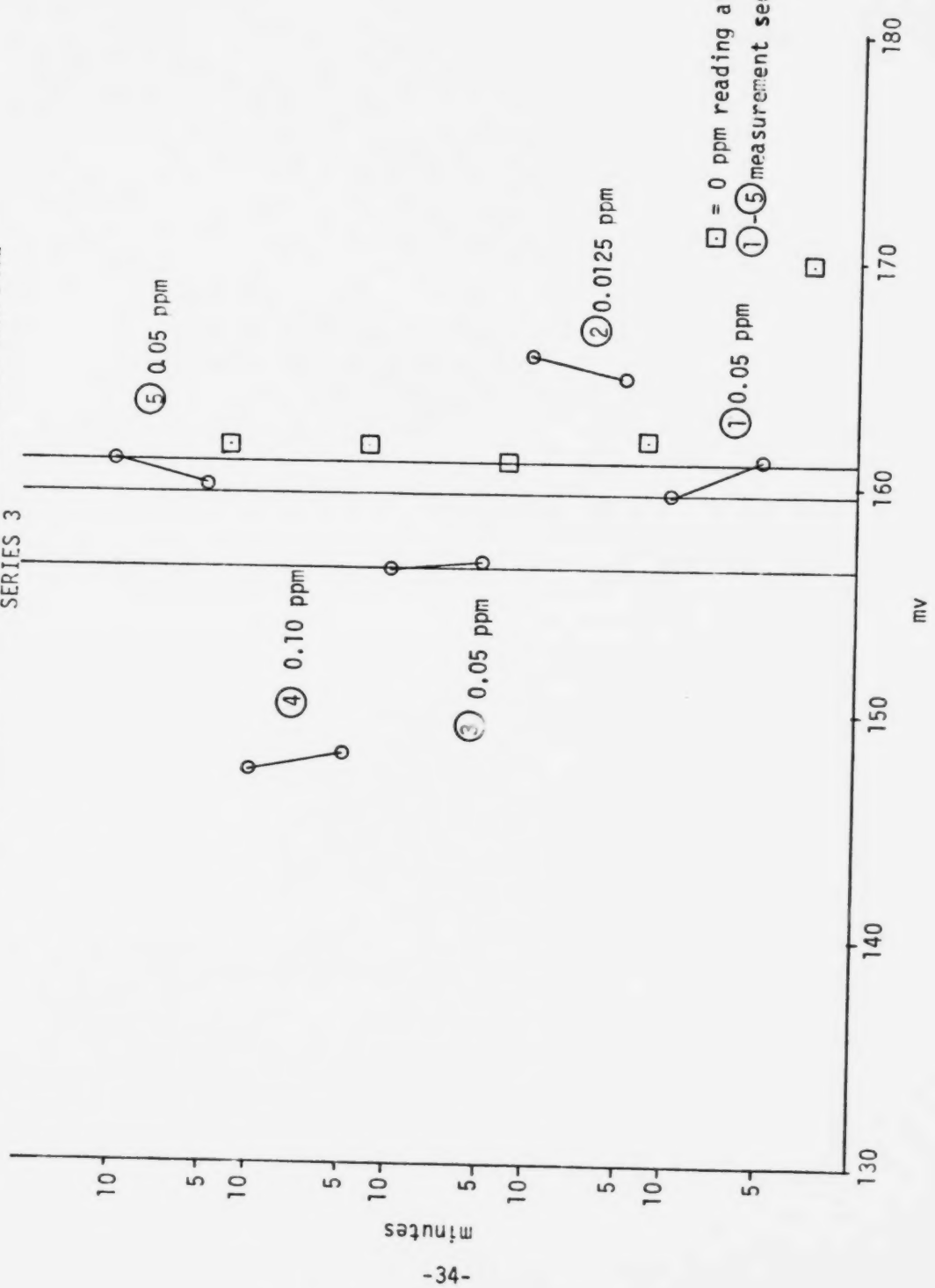


FIGURE 6
EFFECT OF ELECTRODE MEASUREMENT HISTORY UPON RESPONSE
April 27, 1973
SERIES 2
⑤ 0.05 ppm
③ 0.05 ppm
② 0.0125 ppm
④ 0.10 ppm
0.05 ppm ①
□ = 0 ppm reading at 5 min.
①--⑤ measurement sequence
minutes
10
5
mv
130
140
150
160
170
180

FIGURE 7

EFFECT OF ELECTRODE MEASUREMENT HISTORY UPON RESPONSE
SERIES 3
April 30, 1973



range of 4.6 mv which was 3.2 times as great as the variation in series 2. The fact that these three series were done about three days apart with air-conditioned room temperature conditions would not necessarily account for the wide differences in measurement variation ranges among the three series since, within any given series, temperature conditions would be constant among measurement solutions (identical solutions used among the three series-sets). The variation in the arithmetic means of measurement variation ranges for the 0.05 ppm solution may be due to day-to-day room temperature fluctuations. The means for series one, two, and three were 156.4, 151.2 and 158.6, respectively, showing the necessity of recalibration with each group of measurements.

3.2.6.3 Conclusions

Premeasurement electrode conditioning did not affect the variation in a series of measurements at low concentrations and "history effect" was not shown to be an important factor in measurement precision. Since most measurements by direct distillation are low level and closely grouped by predistillation determinations to set the fluoride quantity for distillation near 0.5 mg, "history effect" involving a wide concentration measurement range was not investigated. However, this might be a necessity in the case of high precision measurements on widely varying concentrations in nondistilled sample groups or on distillates from a steam distillation method (fluoride distillation range, 0 to 100 mg).

The procedure of measuring all solutions for a duration of ten minutes had been used prior to this study. This study confirmed its usefulness as a compromise between decreasing mv rates of change with time (increasing precision of measurements) and time per measurement.

3.3 DETERMINATION ON FIELD SAMPLES

3.3.1 DIAMMONIUM PHOSPHATE PLANT

3.3.1.1 Procedure

The A. D. Little Method for sulfuric acid distillation at 210°C with electrode measurement was used for this analysis. The samples collected on January 18, 1973, were obtained using three sample trains operating in each of two separate scrubber outlet ports to yield an estimate of sampling precision. Samples collected January 22, 1973, consisted of the three trains at one outlet port.

Post distillates were collected in addition to sample distillates and were combined to insure complete recovery and to allow a single measurement per sample. Water soluble fluorides only were determined.

3.3.1.2 Discussion of Results

Results are summarized in Table 10. Calculated ppm fluoride stack gas concentrations and statistical analyses are reported in Section IV.

A comparison by the Intersociety Committee Method[3] (perchloric/SPADNS) was not made on these samples due to a change in project orientation by the project officer which discontinued evaluation of the Intersociety Committee versus Arthur D. Little Methods and substituted the C. E. Decker Method (Sulfuric - 180°C/SPADNS) as the primary analysis method to be evaluated.

3.3.2 TRIPLE SUPERPHOPHATE PLANT

3.3.2.1 Purpose and Procedure

The purposes of this experiment were to determine the following: relative error and precision of analysis for stack samples collected January 24, 1973; extent of matrix interference; effects of storage time upon fluoride concentration; and the difference in fluoride measured by SPADNS versus the electrode.

The samples were distilled from sulfuric acid at 180°C as per C. E. Decker, and post distillation was included to insure complete recovery.

3.3.2.2 Discussion of Results

Comparison of SPADNS versus electrode measurements (Table 11) for EPA train runs showed them to be nearly equivalent, with a mean of 97.6 percent, SPADNS to electrode. The FLA train mean of 92.9 percent (P_2R_3 Day 20 was included but not P_2R_3 Day 1 since Day 1 was previously included as P_2R_3 (first and post distillations combined)) was significantly lower, but the small sample sizes precluded a firm conclusion as to whether the difference was attributable to interference differences between the FLA and EPA trains or whether it was due to laboratory error within the SPADNS and electrode methods.

TABLE 10

WATER SOLUBLE FLUORIDES SAMPLING PRECISION ANALYSIS -

DIAMMONIUM PHOSPHATE PLANT, ADL METHOD

Collection Date	Run	Sample Train 1	2	3
1/18/73	1	1.99 mg	2.54 mg	2.71 mg
1/18/73	2	1.30	1.62	2.78
1/22/73	3	2.80	7.15	8.77

TABLE 11

WATER SOLUBLE FLUORIDE MEASUREMENTS - TRIPLE SUPERPHOSPHATE PLANT

Train	Sample	Total F, mg[b]		
		Electrode	SPADNS	SPADNS/Electrode %
FLA	$Port_2$ Run_1	2.54	2.35	92.5
FLA	P_2 R_2	3.44	3.25	94.5
FLA	P_2 R_3	2.95	2.56	86.8
EPA	P_3 R_1	3.30	3.30	100.0
EPA	P_3 R_2	2.45	2.38	97.1
EPA	P_3 R_3	4.07	3.90	95.8
FLA	P_2 R_3[a] Day1	0.84	0.75	89.2 (91.0)[c]
FLA	P_2 R_3[a] Day12	0.84	--	--
FLA	P_2 R_3[a] Day20	0.83	0.81	97.6 (99.8)

[a]Measurement done on first distillate only.

[b]All values uncorrected for background except where indicated.

[c]Value in parenthesis included background corrections.

The P_2R_3 distillation and measurements on aliquots of the sample stored in a polyethylene bottle at room temperature for eleven and nineteen days did not indicate that fluoride loss had occurred.

The standard addition SPADNS data (Table 12) was plotted (Figure 8) and a best-fit line drawn. The matrix interference effect was found by subtracting the mf fluoride value (0.96 mg) for the P_3R_1 aliquot (with no addition of NaF) from the true value (1.10 mg) obtained by the intersection of the best-fit line with the 0 mg fluoride absorbance line (531 mμ). This value was then converted relative to the true value to obtain the Relative Matrix Interference Depression. The matrix interference was thus responsible for a measurement depression of 0.14 mg or 12.7 percent. The potential interfering ions of aluminum, lead, and iron were below levels of detectability and were therefore eliminated as a possible cause for the interference depression determined for these samples.

The relative measurement error for the determination of the true fluoride value (1.10 mg) at the intersection (531 mμ, 1.10 mg F) was found by RE (in percent) =

$$\frac{\Sigma \text{ deviations from the best-fit absorbence line /n.}}{\frac{0.094 \text{ absorbence/mg F}}{1.10 \text{ mg, the true fluoride value}}}$$

RE was calculated to be 1.9 percent. Standard Methods[2] reported a relative error of 2.4 percent for an 830 μg sample analyzed by SPADNS after distillation.

Analysis precision was determined for the electrode measurement made on P_2R_3 Day 1, 12 and 20, since no fluoride loss was evident by either SPADNS or the electrode. The mean value of 0.8367 mg was determined with a precision of 0.0058 mg (the standard deviation) or a relative standard deviation of 0.69 percent.

3.3.3 DEFLUORINATION PLANT

3.3.3.1 Purpose and Procedure

The purpose of these analyses was to determine the following: relative error (accuracy) and relative precision of analysis for total water soluble fluorides (gaseous and particulate); extent of matrix interference effect; and storage time effect both with and without refrigeration in polyethylene bottles.

The sample aliquots were distilled from sulfuric acid at 180°C with a post distillation to insure complete recovery. Measurement and other procedures were equivalent to the C. E. Decker Method.

3.3.3.2 Discussion of Results

3.3.3.2.1 Measurement Precision and Accuracy

The relative standard deviation of 0.28 percent (Table 13) realized in these tests indicates high precision measurements are attainable

TABLE 12

STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS- TRIPLE SUPER PHOSPHATE PLANT

Train Type, Scrubber Outlet Port (Px), Run (Rx) and Fluoride Addition	Absorbence	Total mgF	Relative Error	Relative Matrix Interference Depression
EPA, P_3R_1 + 0.0 mg F	0.428	0.963	1.9%	12.7%
EPA, P_3R_1 + 0.5	0.378	1.435		
EPA, P_3R_1 + 1.0	0.336	1.829		
EPA, P_3R_1 + 1.5	0.286	2.308		

FIGURE 8

STANDARD NaF ADDITIONS FOR INTERFERENCE AND RELATIVE ERROR DETERMINATIONS - TRIPLE SUPER PHOSPHATE PLANT

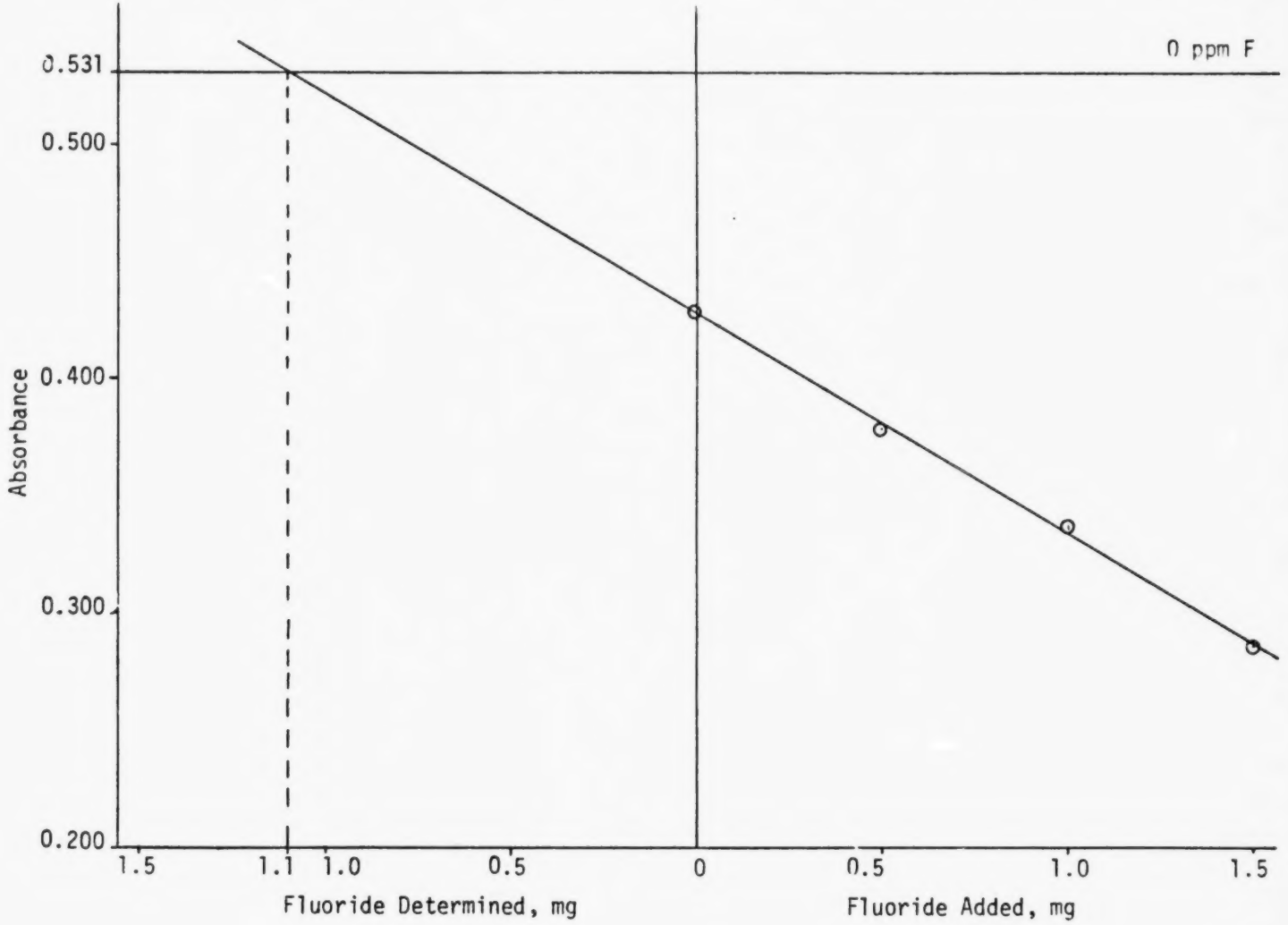


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TABLE 13

WATER SOLUBLE FLUORIDES RELATIVE ANALYSIS PRECISION -
DEFLUORINATION PLANT

Scrubber Port Train Type and Run #	Total mgF	Mean	Standard Deviation	Relative Analysis Precision
Outlet, EPA, Run #2	20.80	21.728 mg	0.06 mg	0.28%
Outlet, EPA, Run #2	21.76			
Outlet, EPA, Run #2	21.76			
Outlet, EPA, Run #2	22.16			
Outlet, EPA, Run #2	22.16			

on this type source of emissions. Relative errors of 0.54 and 1.12 (Table 14) for the inlet and outlet, respectively, were indicators of high accuracy according to Standard Methods[2].

3.3.3.2.2 Inlet and Outlet Matrix Interference and Measurement Accuracy

Standard addition results (Table 14) graphed as previously described, indicated that the scrubber inlet fluorides were determined with a relative matrix interference depression of 5.12 percent (meaning that the total fluoride inlet measurement results were 5.12 percent lower than actuality).

The degree of measurement accuracy (reported as relative error) for the inlet was calculated to be 0.54 percent for a distilled aliquot containing 0.51 mg fluoride.

The outlet fluorides were determined with a relative matrix interference depression of 4.65 percent. This value could have been lowered in relation to the inlet due to matrix interferences having been removed by the scrubber.

Relative error for the outlet determinations was found to be about two times greater than that for the inlet. The distilled aliquot was smaller (0.33 mg) than the 0.51 mg aliquot distilled for the inlet. This fact would probably largely account for the greater average deviation from the best-fit line.

3.3.3.2.3 Inlet and Outlet Water Soluble Fluorides Measurements

Table 15 is a summary of total soluble fluorides found for two measurement procedures; one that did and one that did not include correction for matrix interference.

3.3.3.2.4 Storage Effects

Storage effects data (Table 16) indicated that there was about 10 percent loss of fluoride between day 14* and day 24, whereas, fluorides found for day 24 and 36 were essentially equal. There is suspecion that the sample was not sufficiently capped during this initial period. No loss of fluoride between day 24 and 36 was evidence that fluoride loss due to reaction with bottle materials or internal solution interferences would not be a source of error caused by sample storage.

---

*The day 14 value of 21.73 mg was the mean calculated for the precision data (Table 2). Its associated standard deviation (0.055 mg) was used as an indication of measurement accuracy for the day 24 and 36 refrigerated fluoride measurements. Both of these were higher than two standard deviations (95 percent confidence interval) from the 21.73 mg mean. However, the percentage values relating refrigerated to nonrefrigerated samples were calculated on measurements determined concurrently, so that if errors were due to a measurement bias common to both refrigerated and nonrefrigerated samples, the percentage value would not change significantly, because both results were of roughly the same magnitude.

TABLE 14

STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS - DEFLUORINATION PLANT

Scrubber Port, Train Type, Run # and Fluoride Addition	Total mg F Per Analysis	Relative Error	Relative Matrix Interference Depression
Inlet, EPA, Run #2 + 0 mg F	0.510	0.54%	5.12%
Inlet, EPA, Run #2 + .25 mg F	0.752		
Inlet, EPA, Run #2 + .50 mg F	1.000		
Inlet, EPA, Run #2 + .75 mg F	1.218		
Outlet, EPA, Run #2 + 0 mg F	0.328	1.12%	4.65%
Outlet, EPA, Run #2 + .25 mg	0.580		
Outlet, EPA, Run #2 + .50 mg	0.804		
Outlet, EPA, Run #2 + .75 mg	1.078		

TABLE 15

MATRIX INTERFERENCE EFFECT UPON WATER SOLUBLE FLUORIDES MEASUREMENTS - DEFLUORINATION PLANT

Train and Run #	Uncorrected for Matrix Interference		Corrected for Matrix Interference	
	Inlet gm	Outlet mg	Inlet gm	Outlet mg
EPA 1	15.5	36.3	16.3	38.1
EPA 2	10.7	21.0	11.3	22.0
Fla 1	24.9	25.1	26.2	26.3
Fla 2	7.2	19.0	7.6	19.9

TABLE 16

FLUORIDES STORAGE IN POLYETHYLENE BOTTLES, WITH AND WITHOUT REFRIGERATION AT 45°F - WET PHOSPHORIC ACID PLANT

Stack Port, Train and Run #	Post-Collection Storage Period at Time of Analysis	With Refrigeration	Without Refrigeration	With/ Without
Outlet, EPA 2	14 days	*[1]	21.73 mg	-
Outlet, EPA 2	24 days	22.32 mg	20.08	111.2%
Outlet, EPA 2	36 days	22.24	20.32	109.5%

*[1] The sample was put under refrigeration on day 14.

3.3.4 WET PHOSPHORIC ACID PLANT

3.3.4.1 Purpose and Procedure

The purpose of these analyses was to determine the relative error (accuracy) and relative analysis precision for total water soluble fluorides (gaseous and particulate), extent of matrix interference effect, total water soluble fluorides corrected for matrix interference effect, correlation of fluoride measured prior to and after distillation, and storage time effect both with and without refrigeration in polyethylene bottles.

The samples were taken from the source outlets only. Sample aliquots were distilled from sulfuric acid at 180°C and measurement and other procedures were equivalent to the C. E. Decker Method.

3.3.4.2 Discussion of Results and Conclusions

3.3.4.2.1 Measurement Precision

The relative analysis precision of 1.79 percent (Table 17) was considered indicative of high precision measurements on atmospheric emission fluorides from the outlets samples.

3.3.4.2.2 Matrix Interference and Measurement Accuracy

Standard addition results (Table 18) graphed as previously described, indicated that the scrubber outlet fluorides were determined with a relative matrix interference depression of 15.6 percent (meaning that the total fluoride outlet results were 15.6 percent lower than actuality). The degree of measurement accuracy (reported as relative error) was 0.87 percent for a distilled aliquot containing 0.36 mg fluoride.

3.3.4.2.3 Water Soluble Fluorides Measurements

Table 19 is a summary of total soluble fluorides found for two measurement procedures; one that did and one that did not include correction for matrix interference.

3.3.4.2.4 Measurements Prior to and After Distillation

Table 20 data comparing prior-to-distillation and after-distillation measurements yielded a mean of Prior/After percentage of 103.1 with a standard deviation of 7.44 percent. These results are equivalent (assuming "after" to be the true value, uncorrected for matrix interference) to a relative error of 3.1 percent and relative precision of 7.22 percent. These compare, in the above order, to Standard Methods results for a nondistilled sample of 1.2 and 8.0 percent and a distilled sample of 2.4 and 11.0 percent. It seems likely that these measurements, Prior and After (but uncorrected for matrix interference) distillation, could be treated as equivalents so that distillation would be unnecessary and matrix interference depression corrections as determined on undistilled samples could be applied directly to the measurement obtained on the undistilled samples.

TABLE 17

WATER SOLUBLE FLUORIDES RELATIVE ANALYSIS
PRECISION - WET PHOSPHORIC ACID PLANT

Train Type and Run #	Total mgF	Mean	Standard Deviation	Relative Analysis Precision
Fla-Run #2	58.56	58.75 mg	1.05 mg	1.79%
Fla-Run #2	60.16			
Fla-Run #2	59.20			
Fla-Run #2	57.28			
Fla-Run #2	58.56			

TABLE 18

STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS - WET PHOSPHORIC ACID PLANT

Train and Addition	Total mg F per analysis	Relative Error	Relative Matrix Interference Depression
Fla-Run #2	0.358	0.87%	15.6%
+0.25 mg	0.549		
+0.50 mg	0.740		
+0.75 mg	0.911		

TABLE 19

MATRIX INTERFERENCE EFFECT UPON WATER SOLUBLE FLUORIDES MEASUREMENTS - WET PHOSPHORIC ACID PLANT

Train, Run #, Date			Measurements Uncorrected for Matrix Interference	Measurements Corrected for Matrix Interference
Fla	1	(5/24)	26.8 mg	31.8 mg
EPA	1	(5/24)	42.5	50.4
Fla	2	(5/24)	56.0	66.4
EPA	2	(5/24)	23.3	27.6
Fla	1	(5/25)	158.9	188.3
EPA	1	(5/25)	148.5	175.9

TABLE 20

SPADNS MEASUREMENTS PRIOR TO AND AFTER DISTILLATION -
WET PHOSPHORIC ACID PLANT

Train, Run #, Date	Prior mg F	After mg F	Prior/ After%	Prior/ After % Mean	P/A % Standard Deviation
Fla 1 (5/24)	26.8	26.2	102.3	103.1 %	7.44 %
EPA 1 (5/24)	42.5	37.0	114.9		
Fla 2 (5/24)	56.0	58.8	95.2		
EPA 2 (5/24)	23.3	24.0	97.1		
Fla 1 (5/25)	158.9	145.3	109.4		
EPA 1 (5/25)	148.5	149.0	99.7		

3.3.4.2.5 Storage Effects

Although the two values obtained for refrigerated samples were at a relatively wide variance both among themselves and when compared to the higher precision values in the unrefrigerated category (Table 21), it was concluded, based upon the unrefrigerated values, that no loss had occurred due to sample storage.

3.3.5 PRIMARY ALUMINUM REDUCTION PLANT

3.3.5.1 Purpose and Procedure

The purpose of these analyses was to determine the relative error (accuracy) and relative analysis precision for total water soluble fluorides, extent of matrix interference effect, and storage time effect both with and without refrigeration in glass and in polyethylene bottles. These analyses were completed as per the Environmental Protection Agency, "Method 13 - Determination of Total Fluoride Emissions From Stationary Sources", except that two distillates were collected for each sample to insure complete recovery. Equal aliquots of each distillate were combined to make possible a single measurement per sample.

3.3.5.2 Discussion of Results and Conclusions

3.3.5.2.1 Measurement Precision

The relative standard deviation of 2.4 percent (Table 22) was considered indicative of high precision measurements on samples from this plant.

3.3.5.2.2 Matrix Interference and Measurement Accuracy

Standard addition results (Table 23), graphed as previously described, indicated that the scrubber inlet fluorides were determined with a relative matrix interference depression of 6.15 percent (an average value derived from set 1 and set 2). The negative 2.4 percent relative matrix interference found for the blank correction (standard additions of pure NaF) would increase the 6.15 percent value, above, to 8.55 percent, if applied. These single matrix interference depression measurements should be used with the knowledge that seven or eight repetitions of such sets would provide a measure of the degree of precision for this method of standard addition, according to, L. L. Ingvar, et al (6) N. A. Hartman and J. J. Wagner, "Estimating Precision for the Method of Standard Additions," Anal. Chem., 45, 1511-1513 (July, 1973)[6]. This publication, described the determination of precision estimates for values both with and without blank corrections. The EPA Method 13 does not include provisions for blank corrections. Method 13 reported a 3 percent relative standard deviation on a set of twenty replicate intralaboratory determinations on a stack emission sample. Also cited as evidence of Method 13 procedural adequacy were the following statements: "A phosphate rock standard containing a certified value of 3.84 percent fluoride was analyzed by this procedure. The average of five determinations was 3.88 percent fluoride." The relative error was, therefore,

TABLE 21

FLUORIDES STORAGE IN POLYETHYLENE BOTTLES, WITH AND WITHOUT REFRIGERATION AT 45°F - WET PHOSPHORIC ACID PLANT

Train and Run #	Post-Collection Storage Period at Time of Analysis	With Refrigeration	Without Refrigeration
Fla 2	10 days	*	58.8 mg
	31 days	56.0	58.4 mg
	47 days	61.9	59.5 mg

* The sample was put under refrigeration on day 10.

TABLE 22

WATER SOLUBLE FLUORIDES RELATIVE ANALYSIS
PRECISION - ALUMINUM REDUCTION PLANT

Train Solution	Total mg F per equal aliquot	Mean	Standard Deviation	Relative Analysis Precision
EPA1 - Run 1	0.5375	0.5405	0.0131	2.42%
EPA1 - Run 1	0.5488			
EPA1 - Run 1	0.5488			
EPA1 - Run 1	0.5488			
EPA1 - Run 1	0.5188			

TABLE 23

STANDARD NaF ADDITIONS TO DETERMINE MATRIX INTERFERENCE AND RELATIVE ERROR OF ANALYSIS - ALUMINUM REDUCTION PLANT

Train and Fluoride Addition	Total mg F per Analysis	Relative Error, %	Relative Matrix Interference Depression
EPA1 Run #1	0.5188	1.0	7.3%
+0.25 mg	0.7813		
+0.50 mg	0.9750		
+0.75 mg	1.2025		
EPA1 Run #1	0.5738	5.1	5.0%
+0.25 mg	0.8900		
+0.50 mg	1.0563		
+0.75 mg	1.2813		
+1.00 mg	1.4750		
	Blank Correction		
0.500 mg NaF	0.525	5.0	-2.4%
+0.25 mg	0.819		
+0.50 mg	1.029		
+0.75 mg	1.275		
+1.00 mg	1.440		

1.04 percent. Accuracy determination for the unknown stack emission sample could be determined by a standard addition method as used in these experiments, and further detailed as to standard addition method precision determination by Ingvar[6]. No relative precision of measurement was cited for the phosphate rock sample, above.

The degree of measurement accuracy (reported as relative error) was 1.0 percent for determination set 1 and 5.1 percent for set 2 for an average of 3.05 percent. Relative error calculated for the blank correction was 5.0 percent.

Analytical tests for aluminum and silicate yielded inlet impinger solution concentrations of 41 ppm and 10 ppm, respectively, for the Fla. train. These are well below the 300 ppm level for both cited by ASTM: D1179-68 as necessary to retard distillation.

3.3.5.2.3 Water Soluble Fluoride Measurements

Table 24 is a summary of total fluorides corrected for a 6.2 percent matrix interference depression. The engineering significance of these measurements is reported in Section IV.

3.3.5.2.4 Water Insoluble Fluoride Measurements

Water insoluble fluorides (Table 24) were collected on paper filters and treated according to Method 13 procedures. Only a few were done to test the procedure since remaining project time was short.

Method 13 specifies that the Whatman #541 filters should be macerated by glass rod in nickel crucibles containing a few ml of water. This was found to be unworkable even after standing with water overnight. The glass rod should be replaced by tweezers, to shred the filter.

3.3.5.2.5 Storage Effects

Although some experimental bias was evident, wherein 39-day measurements were higher than those at 24 days and slightly lower than at 12 days, it was concluded that effects of storage were negligible within the refrigerated and nonrefrigerated groups. Glass storage in both refrigeration categories was essentially equivalent to storage in polyethylene bottles. Samples refrigerated in glass and polyethylene containers were each concluded to be not over 1 1/2 percent higher than nonrefrigerated samples in glass and polyethylene containers.

TABLE 24

TOTAL FLUORIDES MEASUREMENTS CORRECTED FOR 6.2 PERCENT
MATRIX INTERFERENCE DEPRESSION - ALUMINUM REDUCTION PLANT

Sample Collection Date	Train	Port	Run #1, mg F	Run #2, mg F	Run #3, mg F
Water Soluble Fuorides					
6/11/73	EPA #1	Inlet	90.8	88.5	99.2
	EPA #2		74.5	31.3	88.8
	EPA #3		71.9	77.5	83.1
6/12/73	FLA	Inlet	107.2	134.7	98.8
	EPA Probe		18.0	17.7	24.5
	EPA Impinger #1		72.7	68.7	65.9
	EPA Impinger #2		18.2	14.9	20.6
	EPA Impinger #3		10.5	7.6	1.9
6/13-14/73	EPA	Outlet	36.2	27.9	47.9 (6/14/73)
	FLA	Outlet	16.4	37.7	29.2 (6/14/73)
Water Insoluble Fluorides					
6/12/73	EPA Probe	Inlet	0.8 mg.		
	EPA Impinger #1 and #2	Inlet	0.4 (Impinger #1 and #2 combined)		
	EPA Impinger #3	Inlet	0.1		

TABLE 25

FLUORIDES STORAGE IN GLASS AND POLYETHYLENE BOTTLES, WITH AND WITHOUT REFRIGERATION (45°F) - ALUMINUM REDUCTION PLANT

Sample	Container	Post-Collection Storage Period at Time of Analysis	With Ref., mg.	Without Ref., mg
EPA, Impinger #1, Run #1	Polyethylene	12 days	*1	68.23
	Polyethylene	24 days	65.31	64.30
	Glass	24 days	66.80	65.70
	Polyethylene	39 days	67.97	67.97
	Glass	39 days	73.44	67.58

*1 Sample was put under refrigeration on day 12.

4.0 FIELD ACTIVITIES

4.1 INTRODUCTION

Four plants characterizing four different processes were visited during the project. Although three of the plants which were tested processed phosphate rock, each plant was tested for a different process. The phosphate processes tested were; a diammonium phosphate (DAP) scrubber outlet, a rotary defluorination kiln scrubber and a set phosphoric acid plant scrubber. The fourth and final plant visited was an aluminum reduction facility in which the scrubber inlet and outlet were tested.

4.2 SUMMARY

Table 26 presents a summary of results for the various plants tested. Examination of this table reveals considerable variation not only between the Florida and EPA collection methods, but between individual EPA trains as well. Of 18 tests in which the Florida and EPA collection trains were compared, the former gave lower results on 11 of the tests (61 percent). For these same 18 tests, the EPA method gave results that were 16 percent higher than the Florida train on an average, the range being from 62 percent lower (Run #2, May 25) to 101 percent higher (Run #1, June 13).

Comparing the data for the three EPA trains operating simultaneously with the mean for each run, one finds a range of 53 percent below the mean (EPA 2, Run #2, June 11) to 34 percent above the mean (EPA 3, Run #2, January 18). While this range may seem quite large, the following observations are appropriate. On the low end of the concentration range (found in the DAP process), which was approximately 1 - 2 parts per million (ppm) as HF, differences between individual trains (operators, meter calibrations, etc.) will account for a large amount of variation. With concentrations that were higher, found at the scrubber outlet of the aluminum reduction plant, variation between trains was not nearly so great. Considering the data from EPA 2, Run #2 June 11 as "bad" data and eliminating it, alters the range from 53 to 38 percent below the mean.

4.3 SAMPLING PROCEDURES

For those tests in which three EPA trains were operated simultaneously, the probes were placed in the stack so that the nozzles of all three were as close together as possible. For tests utilizing one EPA and one Florida train, the two probes were attached together with a common pitot tube. In this way, it was hoped to minimize error introduced by any concentration gradient within the stack.

Prior to performing the actual tests, it was necessary to determine the following stack parameters: average temperature, average velocity head, and moisture content. Where possible, these were obtained from

TABLE 26

FLUORIDE CONCENTRATION SUMMARY

Plant	Process	Date	Run	ppm V/V Dry for Indicated Train				
				Florida	EPA 1	EPA 2	EPA 3	Mean
Fertilizer	DAP Scrubber Outlet [a]	12/20/72	1	1.01	1.38			1.19
		12/21/72	2	1.55	2.79			2.17
		1/18/73	1		1.31	1.44	1.59	1.45
			2		0.81	0.81	1.30	0.97
		1/22/73	3		1.79	3.40	3.41	2.87
		1/24/73	1	1.17	1.62			1.40
			2	1.51	0.96			1.24
			3	1.54	1.46			1.50
	Defluorination Kiln Scrubber Outlet [b]	5/8/73	1	13.60	18.00			15.80
			2	10.60	18.60			14.60
	Kiln Scrubber Inlet [b]	5/9/73	1	20,288	11,702			15,995
			2	6,577	8,400			7,488
Phosphoric Acid	Wet Phosphoric Acid Scrubber Outlet [b]	5/24/73	1	12.60	17.20			14.90
		5/25/73	2	36.40	14,00			25.20
			3	83.90	82.40			83.20

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TABLE 26 (continued)

FLUORIDE CONCENTRATION SUMMARY

Plant	Process	Date	Run	ppm V/V Dry for Indicated Train				
				Florida	EPA 1	EPA 2	EPA 3	Mean
Aluminum Reduction	Scrubber Inlet[b]	6/11/73	1		108.5	93.9	94.4	98.9
			2		106.0	38.3	99.1	81.1
			3		118.5	111.6	104.8	111.6
		6/12/73	1	131.4	141.4			136.4
			2	165.3	127.2			146.2
			3	119.6	131.7			125.6
	Scrubber Outlet[b]	6/13/73	1	10.1	20.3			15.2
			2	19.6	13.1			16.4
		6/14/73	3	25.5	36.5			31.0

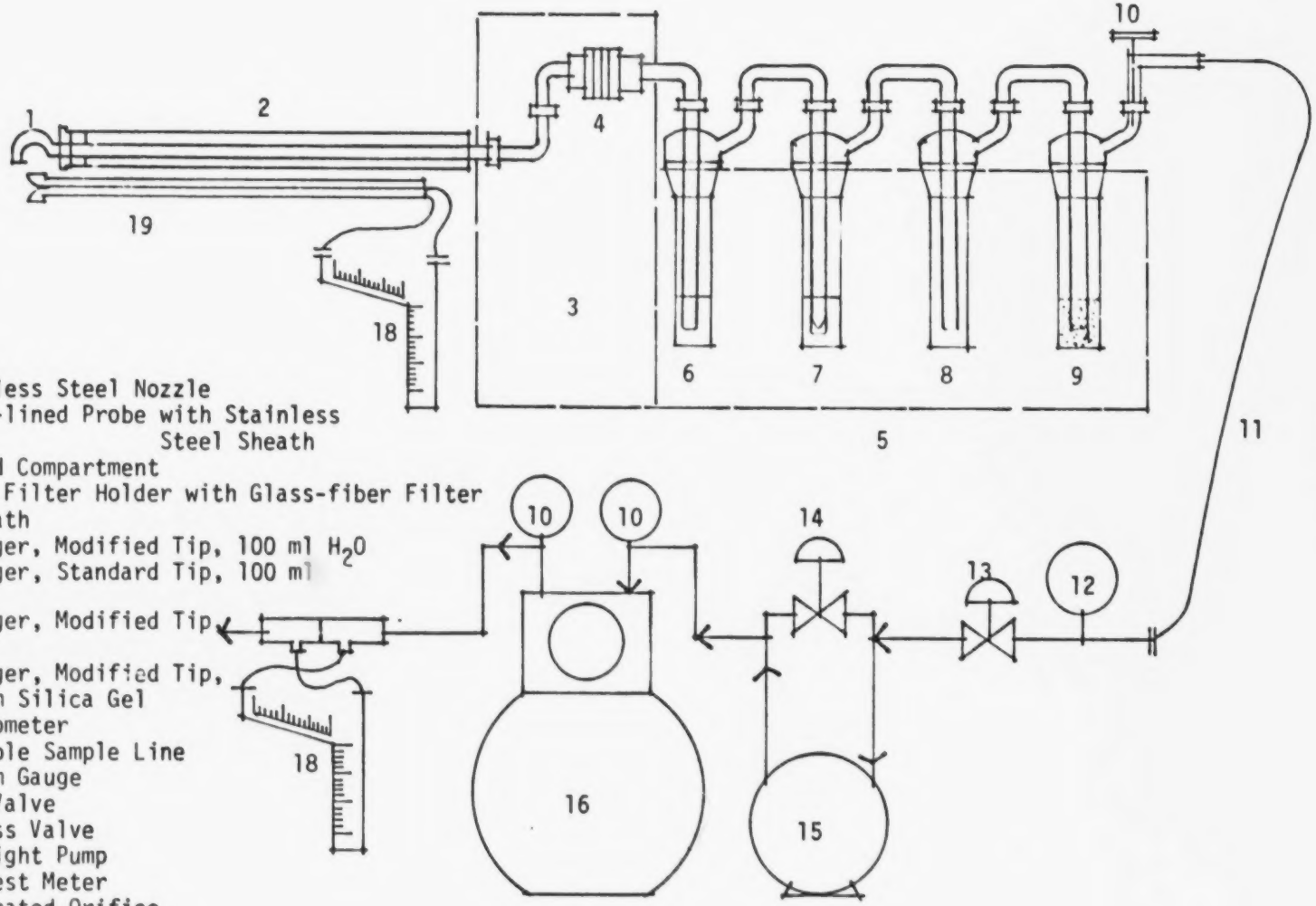
[a] Lab analysis by specific ion electrode
[b] Lab analysis by SPADNS

plant personnel except the average stack gas temperature which was determined with a biemetallic dial type thermometer and monitored throughout each test. When this information was not available, the average velocity head was found by making a traverse of the stack with a calibrated "S" type pitot tube and inclined manometer prior to the test. Moisture content of the stack gases was then estimated from a 15-minute pre-run using the collection train.

For the first sampling trip to the DAP facility, the EPA sampling train consisted of the following equipment: a stainless steel nozzle; a glass-lined probe; a Gelman Type "A" glass fiber filter; two Greenburg-Smith impingers, each containing 100 ml deionized water; one dry impinger; one impinger containing about 200 grams of silica gel (the first, third, and fourth impingers had modified tips with 1/2-inch I.D. openings, the second impinger had a standard tip); a thermometer on the fourth impinger; flexible sampling line; air-tight pump; dry test gas meter; and a calibrated orifice with inclined manometer attached. Figure 1 is a schematic diagram of the sampling train.

At a meeting between the EPA project officer and project personnel from ESE on February 2, 1973, the EPA sampling train was changed. Following this date, the train consisted of: a stainless steel nozzle; glass-lined probe: three Greenburg-Smith impingers, each containing 100 ml deionized water; one dry impinger; a Gelman Type "A" glass fiber filter; the remainder of the train being unchanged. Figure 2 is a schematic diagram of this sampling train.

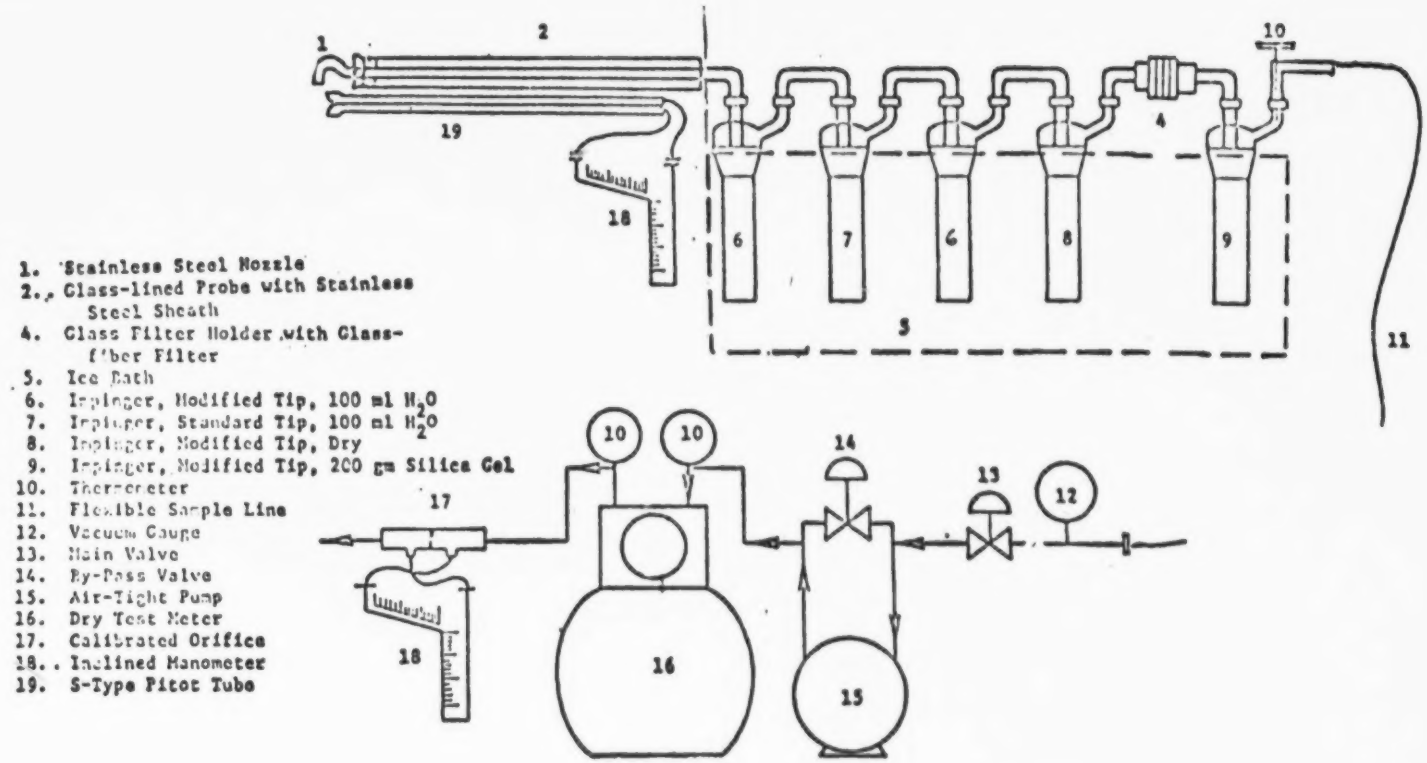
The modified Florida train consisted of: a stainless steel nozzle and probe; two Greenburg-Smith impingers, each containing 100 ml deionized water; one dry impinger; one impinger containing 200 grams of silica gel; the remainder of the train consisting of the same equipment found on the EPA train. The only other difference between the Florida and revised EPA trains was the lack of an ice bath on the condenser section of the Florida train. Figure 3 is a schematic diagram of this train.



1. Stainless Steel Nozzle
2. Glass-lined Probe with Stainless Steel Sheath
3. Heated Compartment
4. Glass Filter Holder with Glass-fiber Filter
5. Ice Bath
6. Impinger, Modified Tip, 100 ml H_2O
7. Impinger, Standard Tip, 100 ml H_2O
8. Impinger, Modified Tip Dry
9. Impinger, Modified Tip, 200 gm Silica Gel
10. Thermometer
11. Flexible Sample Line
12. Vacuum Gauge
13. Main Valve
14. By-Pass Valve
15. Air-Tight Pump
16. Dry Test Meter
17. Calibrated Orifice
18. Inclined Manometer
19. S-Type Pitot Tube

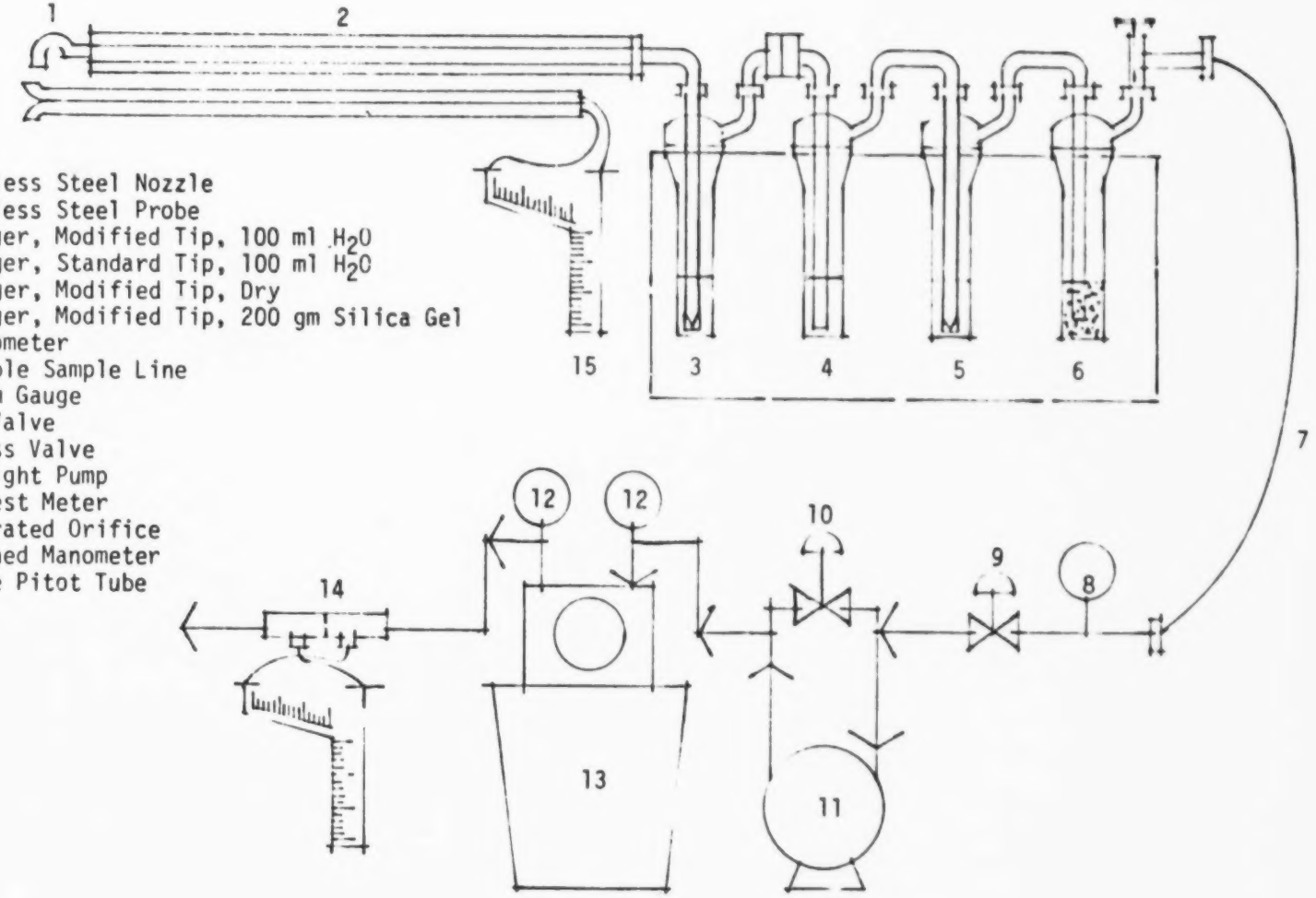
EPA Method 5 Particulate Sampling Train

FIGURE 1


1. Stainless Steel Nozzle
2. Glass-lined Probe with Stainless Steel Sheath
4. Glass Filter Holder with Glass-fiber Filter
5. Ice Bath
6. Impinger, Modified Tip, 100 ml H_2O
7. Impinger, Standard Tip, 100 ml H_2O
8. Impinger, Modified Tip, Dry
9. Impinger, Modified Tip, 200 gm Silica Gel
10. Thermometer
11. Flexible Sample Line
12. Vacuum Gauge
13. Main Valve
14. By-Pass Valve
15. Air-Tight Pump
16. Dry Test Meter
17. Calibrated Orifice
18. Inclined Manometer
19. S-Type Pitot Tube

Proposed EPA Fluoride Sampling Train

Figure 2



Modified Floride Train

FIGURE 3

5.0 COLLECTION EFFICIENCY STUDY

The approach taken for determing the collection efficiency of the EPA train was simply to meter a known concentration of hydrogen fluoride (HF) into the collection train for a period of time similar to field conditions. Knowing both flow rate and concentration, the amount of HF metered into the impingers could be determined. Collection efficiency was then defined as:

$$\% \text{ Efficiency (percent)} = \frac{\text{grams HF recovered}}{\text{grams HF in}} \times 100\% \quad (1)$$

The original set-up for this laboratory study is shown in Figure 9. Undiluted HF was to have been metered through a mass flowmeter calibrated from 0 - 10 ml/min. This then was to have been diluted with nitrogen to the desired concentration and bubbled through the collection train. This scheme failed when the mass flowmeter clogged and no satisfactory repair could be obtained from the supplier.

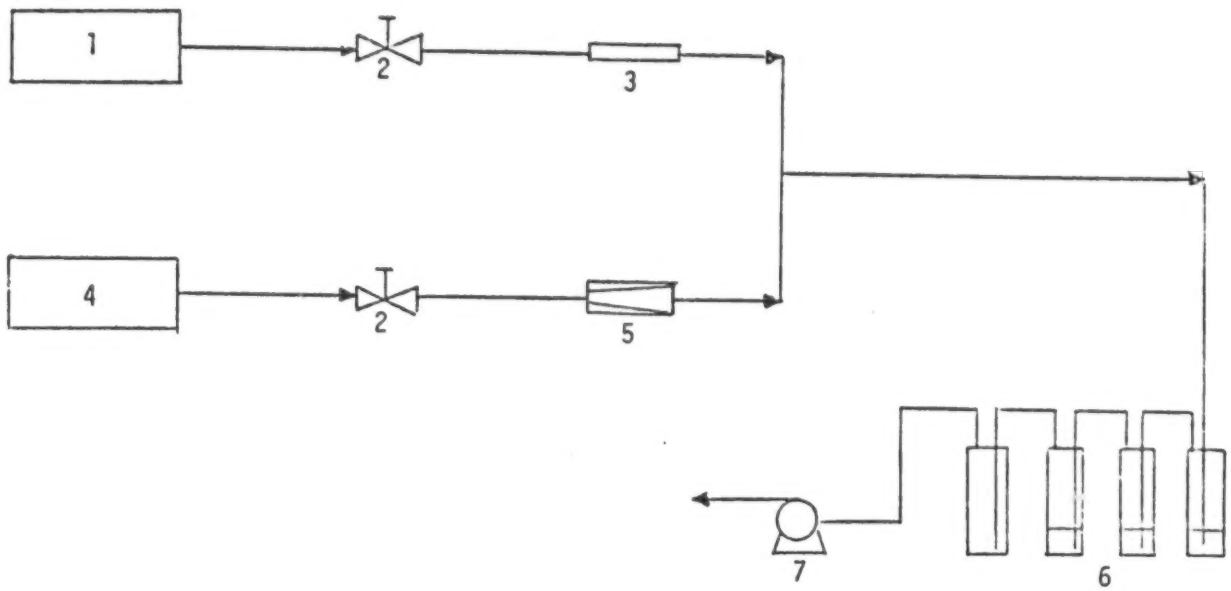
Upon considering the problems mentioned above, a dilution system was suggested consisting of a low concentration of HF in nitrogen prepared in a passivated stainless steel pressure tank.

Mixtures of HF in nitrogen were made in a stainless steel oxygen tank which had previously been passivated with HF. The procedure was as follows: the tank was well flushed with dry nitrogen and evacuated to about -26 in. Hg abs with a vacuum pump. Vacuum was measured with a mercury U-table manometer. A small amount of HF was then admitted to the evacuated cylinder and another vacuum reading was made using the manometer. The tank was then pressurized with dry nitrogen. After the contents had reached thermal equilibrium with the surroundings (about 30 minutes was allowed) a pressure reading was obtained using a calibrated gauge accurate to 0.2 PSIG. The HF concentration was then determined as the partial pressure of HF in the tank divided by the total tank pressure absolute. Mixtures made in this fashion ranged from 0.8 to 1.5 percent HF (see Figure 10).

The mixture from the tank was metered through a stainless steel needle valve and calibrated orifice to a tee where it was further diluted with nitrogen which was metered through a rotameter. Tne tee then led to the impinger train. A vacuum pump was attached to the outlet of the impinger train to simulate field operation and was operated between -1 to -10 in. Hf abs Figure 10 is a schematic of the experimental set-up.

Twelve experimental runs were made, Nos. 1-7 being two hours in length, the remainder being of one hour duration. At the end of a run each impinger was well rinsed with distilled water and the contents analyzed for fluoride using a specific ion electrode. Tota! fluoride recovered

FIGURE 9
FIRST EXPERIMENTAL SET-UP FOR COLLECTION EFFICIENCY STUDY



1. 100% HF
2. Control Valve
3. Linear Mass Flowmeter
4. N_2
5. Rotameter
6. Impinger Train
7. Vacuum Pump

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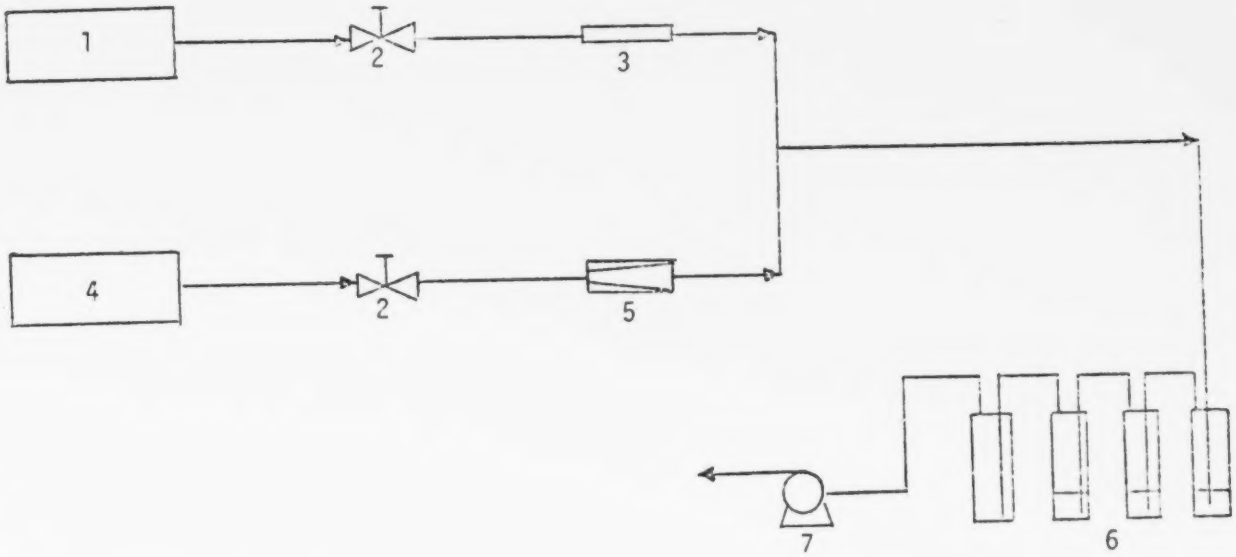
FIGURE 10
SECOND EXPERIMENTAL SET-UP FOR COLLECTION EFFICIENCY STUDY



1 HF Dilution Tank
2 Control Valve
3 Calibrated Orifice
4 N_2
5 Rotameter
6 Impinger Train
7 Vacuum Pump

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was then the sum of the fluoride in the three impingers plus that found in the distilled water rinse of the fourth impinger and connecting U-tubes.

Total fluoride put through the impinger train was determined from the following equation:

$$HF\ (grams) = \frac{Q \times t \times C \times 0.244 \times 10^{-6}}{T}$$

Where: Q = Average volometric flow rate of HF mixture from dilution tank; measured by calibrated orifice ml/min.

t = Total time of run, minutes

c = HF concentration in dilution tank ppm

T = Ambient temperature °K

$$0.244 = 20.006 \frac{g}{g\text{-mole}} \times \frac{273\ °K}{22{,}414\ cc/g\text{-mole}}$$

Collection efficiency was then defined as g. HF recovered ÷ g. HF in x 100.

Table 27 is a summary of findings for 13 runs. It should be noted that there is considerable scatter in the results, which is attributed to adsorption and/or reaction of HF with the stainless steel dilution tank.

In an attempt to determine if this was the problem a mass balance was made over the entire system. In doing this the dilution tank was first well rinsed with distilled water to insure removal of any absorbed HF. After this it was rinsed with acetone and flushed with nitrogen to insure that the tank was well dried. A mixture was then made using the method previously described and a one hour run performed. After the run, the tank pressure was measured and the remaining contents vented to the atmosphere through an outside scrubber. The dilution tank was then rinsed with twelve 250 ml portions of distilled water to capture any adsorbed HF. The concentration of HF in the tank; as determined by partial pressures, was then modified my multipling by the fraction of HF unadscrbed in the tank divided by the total HF put into the dilution tank.

By following the above procedure it was possible to account for 98.5 percent of the HF put into the dilution tank. The subsequent collection efficiency was determined as 53.9 percent.

While the collection efficiencies showed much scatter and were generally lower than expected, the following evidence indicates that collection efficiencies should be higher. The data for each run were analyzed by

TABLE 27
COLLECTION EFFICIENCY STUDY FOR HF

Run	Date	Absorbing Reagent	Flow Rate	Concentration	Total HF into Impingers g	Total HF Recovered	% Recovery(1)
1	3/2/73	water	1 CFM	100 ppm	0.288	0.2469	85.7
2	3/5/73			S C R U B B E D			
3	3/6/73	water	0.5 CFM	100 ppm	0.142	0.1360	95.8
4	3/6/73	0.1N NaOH	0.5 CFM	100 ppm	0.138	0.0999	72.4
5	3/7/73	0.1N NaOH	1 CFM	100 ppm	0.222	0.1642	74.0
6	3/7/73	0.1N NaOH	1 CFM	100 ppm	0.184	0.1390	75.5
7	3/8/73	water	1 CFM	45 ppm	0.122	0.0945	77.5
8	3/9/73	water	1 CFM	50 ppm	0.068	0.0518	76.2
9	4/3/73	water	1 CFM	100 ppm	0.125	0.0524	41.9
10	4/5/73	water	0.3 CFM	8 ppm	0.0031	0.0044	142.0
11	4/5/73	water	1 CFM	2 ppm	0.0024	0.0021	87.6
12	4/5/73	water	1 CFM	2 ppm	0.0027	0.0010	38.4
13	4/11/73	water	1 CFM	20 ppm	0.0246	0.0133	53.9

(1) g HG recovered ÷ g Hf in x 100%

expressing the amount recovered in each impinger as a percentage of the total recovered which was remaining after the previous impinger(s). The following example should clarify this:

Sample	Total Fluoride found g
Impinger 1	0.5
Impinger 2	0.1
Impinger 3	0.01
U-Tube	0.001

A total of 0.611 fluoride was recovered. Of this, 0.5/0.611 = 82 percent was recovered in the first impinger. Of the remaining fluoride, 0.611 - 0.500 = 0.111, 0.1 was captured by the second impinger or 0.1/0.111 = 90 percent of the fluoride remaining after passing through the first impinger was captured in the second impinger. Table 28 is a summary of the data analyzed in this fashion for the experimental runs made. For the 11 runs in which the data was analyzed, an average of 89.6 percent of the HF recovered was found in the first impinger. Of the remaining, an average of 84.1 percent was caught in impinger No. 2 and an average of 64.4 percent of the HF caught after impingers 1 & 2 was in impinger No. 3. These data intuitively suggest that the actual collection efficiency of this train is approximately 90 percent. The low percentage caught in the 3rd impinger might possibly be explained by the very low concentration of HF in the gas flowing to this impinger.

After reviewing the foregoing data it was felt that this method for obtaining mixtures of HF in nitrogen was unreliable.

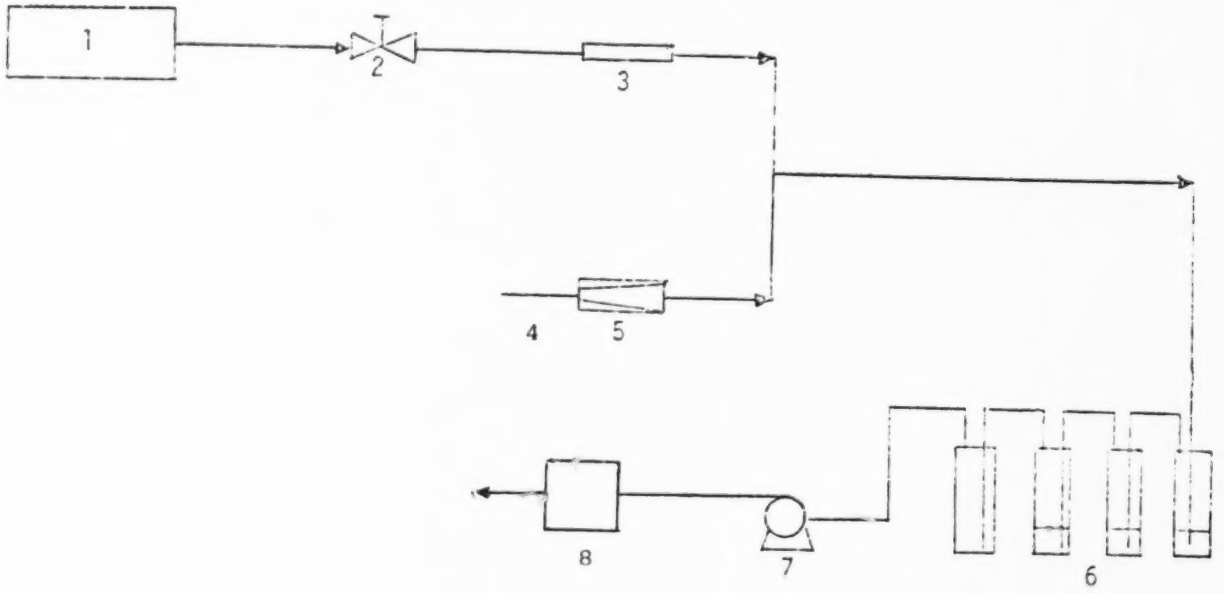
The final approach to obtaining reliable mixtures was to purchase a dilute mixture of HF in nitrogen from a gas supplier in a plastic lined cylinder. The same experimental procedure was used as previously described with the exception of mixing 17 dilutions. The dilution tank in Figure 10 was therefore replaced by a certified HF mixture containing 1.15 percent HF in Nitrogen obtained from Matheson Gas Company. Also a dry gas meter was added after the vacuum pump. A schematic diagram of the final experimental configuration is included in Figure 11. Sixteen experimental runs were made, each being one hour in duration. The following parameters were varied: flow rate, concentration, and pH of the absorbing reagent. The absorbing reagents chosen were distilled water and 0.1 N NaOH, the concentration range from 10 - 100 ppm, and the flow rates 1 and 0.75 cfm. Table 29 is a summary of these findings.

The large variance in the collection efficiencies for the different experimental runs prompted an investigation. As the efficiencies appeared to directly proportional to concentration, graphs were prepared of collection efficiency versus concentration; these are presented in Figures 12 and 13. Figure 12 is for those experimental runs in which

TABLE 28
% REMAINING FLUORIDE RECOVERED

Run	1st Impinger	2nd Impinger	3rd Impinger
1	95.9	94.3	85.3
3	93.3	94.9	72.5
4			
5	94.2	86.4	41.1
6	95.2	97.3	28.0
7	89.4	96.3	68.9
8	90.4	93.6	72.5
9	89.7	94.3	79.1
10	72.7	12.6	96.7
11	81.9	79.2	55.9
12	91.2	83.2	45.8
13	91.4	92.9	62.3
Avg.	89.6	84.1	64.4

FIGURE 11
FINAL EXPERIMENTAL SET-UP FOR COLLECTION EFFICIENCY STUDY



1. 1% HF in Nitrogen
2. Control Valve
3. Calibrated orifice
4. Clean Air
5. Rotameter
6. Impinger train
7. Vacuum Pump
8. Dry gas meter

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TABLE 29
HF COLLECTION EFFICIENCIES

Run	Date	Absorbing Reagent	Flow Rate cfm	Concentration ppm V/V	Total HF into Impingers g	Total HF Recoverd g	% Recovery(1)
1	5/16/73	Dist. H_2O	1	82	0.1109	0.0640	57.6
2		"	1	80	0.1082	0.0738	68.2
3		"	1	79	0.1080	0.0838	77.6
4	5/17/73	"	0.75	90	0.0967	0.0663	68.6
5		"	0.75	85	0.0934	0.0754	80.8
6	5/21/73	"	1	11	0.0160	0.0051	31.7
7		"	1	11	0.0143	0.0053	37.1
8	5/22/73	"	0.75	9	0.01017	0.00438	43.1
9	6/05/73	0.1 N NaOH	1	35	0.04853	0.03378	69.6
10		"	1	71	0.10076	0.09397	93.3
11		"	1	63	0.09939	0.10172	102.3
12	6/6/73	"	0.75	95	0.10273	0.09158	89.1
13		"	0.75	92	0.10095	0.09208	91.2

(1) g HF recovered ÷ g HF in x 100%

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TABLE 29
HF COLLECTION EFFICIENCIES

Run	Date	Absorbing Reagent	Flow Rate cfm	Concentration ppm V/V	Total HF into Impingers g	Total HF Recovered g	% Recovery(1)
14	7/25/73	0.1 N NaOH	1	68	0.10920	0.06487	59.4
15		"	0.75	96	0.10030	0.06840	95.8
16	7/26/73	"	1	10	0.01393	0.00630	45.2
17		"	0.75	9	0.01008	0.00455	45.1

FIGURE 12

COLLECTION EFFICIENCY VS CONCENTRATION
DISTILLED WATER

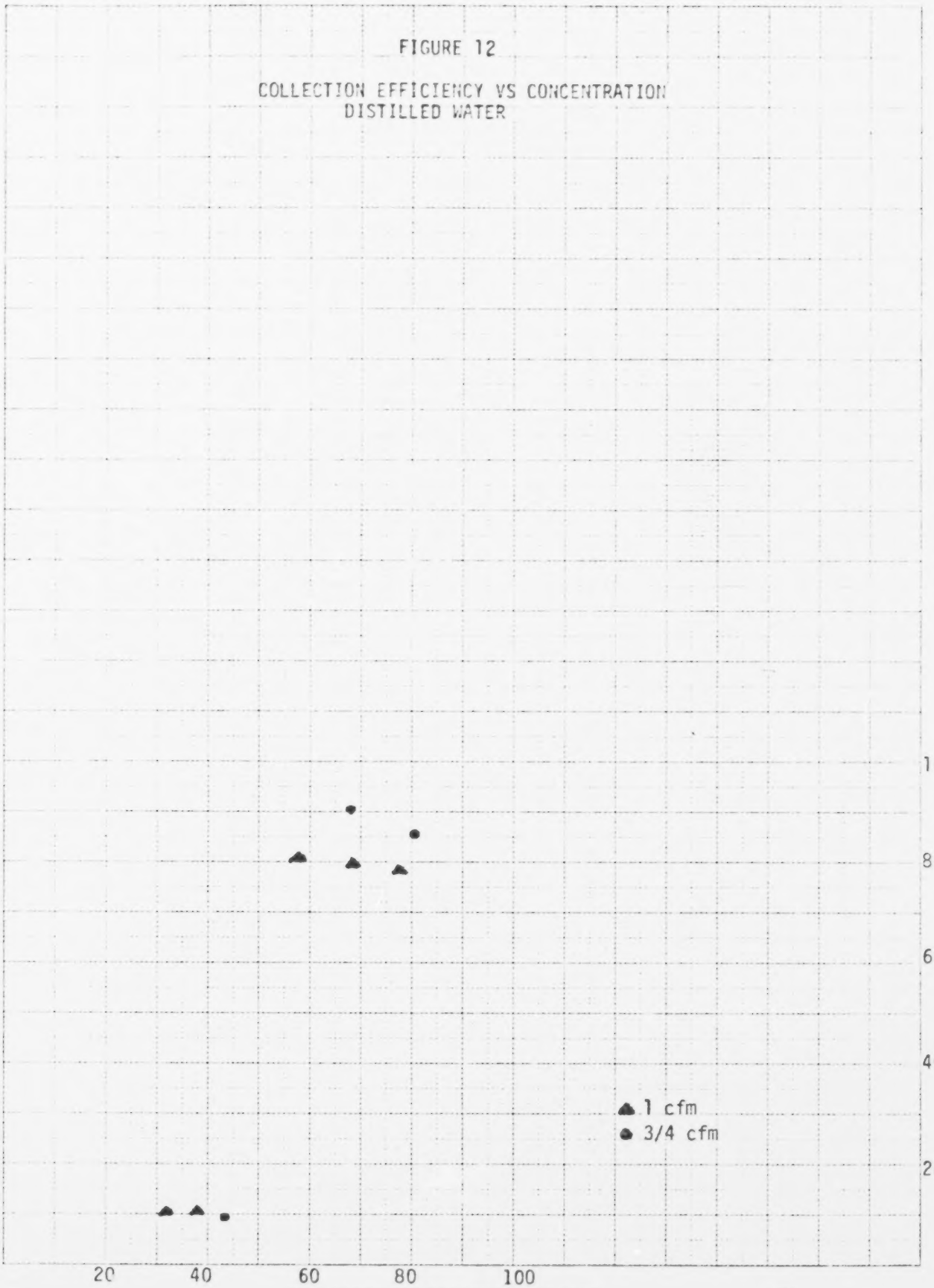
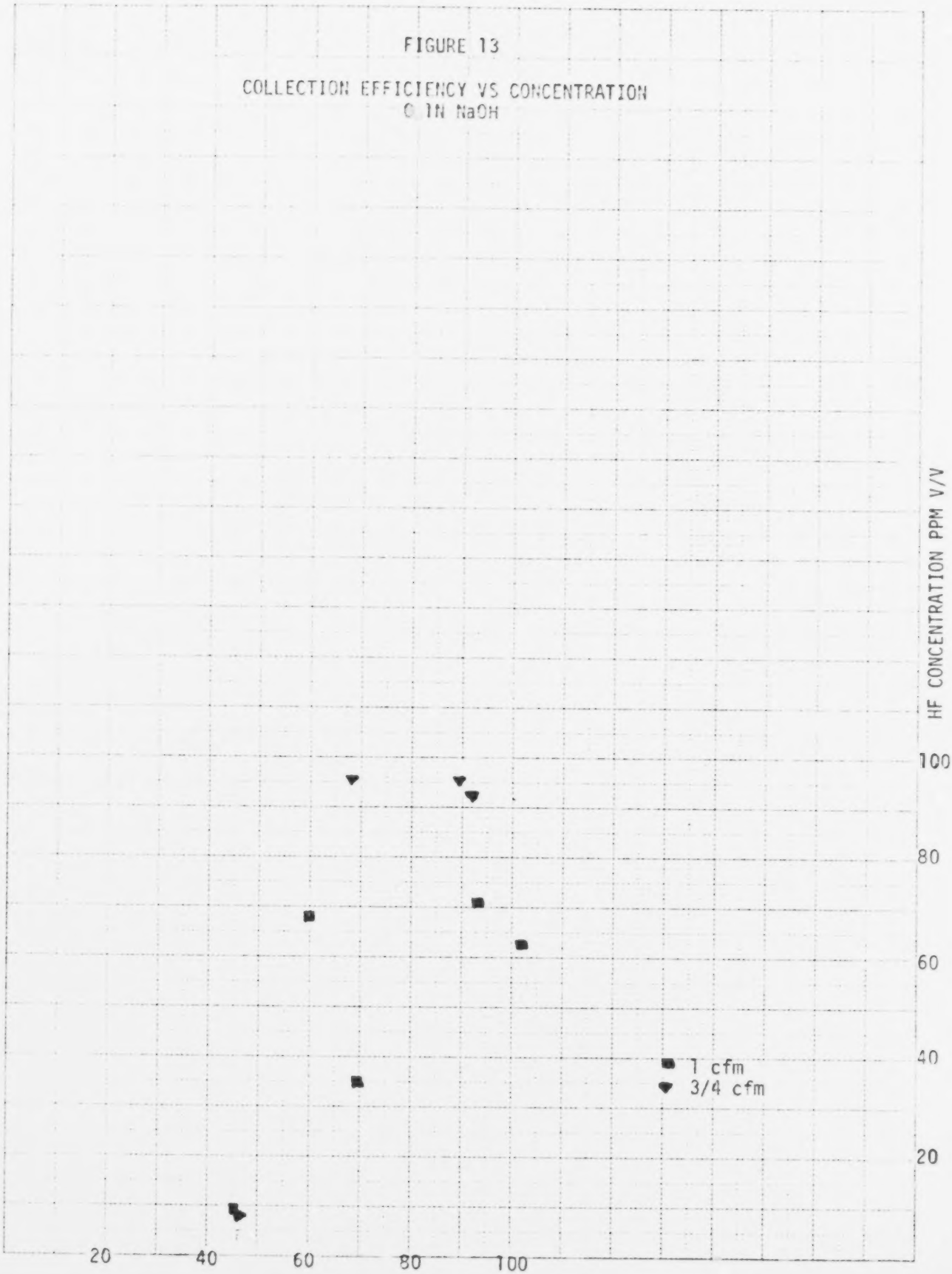


FIGURE 13

COLLECTION EFFICIENCY VS CONCENTRATION
0.1N NaOH



water was used as the absorbing reagent and Figure 13 for those in which sodium hydroxide was used. Examination of these two figures reveals the following. First, there appears to be no significant difference between the efficiencies in which sodium hydroxide was used and those in which water was used. Second, the collection efficiency appears to be directly proportional to the concentration of the gases being measured. The first observation was borne out by statistical analysis of the data which indicated no significant difference between the two absorbing solutions (F=2.54). Table 30 presents a summary of these statistics.

The average collection efficiency for all of the runs using water as the absorbing reagent was 58.1 percent the corresponding value for 0.1N NaOH was the absorbing reagent was 76.8 percent.

In a similar study, Dorsey and Kemnitz[5] found an average collection efficiency for HF to be 90.7 percent for 12 runs at concentrations ranging from 0 - 4000 ppm with a flow rate of 0.75 cfm using 0.1N sodium hydroxide[1]. While this value is somewhat higher than the value of 73.4 percent found for four runs at the same conditions, it is not known at this time how many runs they made with a concentration between 10 and 100 ppm. As was illustrated earlier, the efficiency dropped off in direct proportion to the concentration. Two runs made at about 100 ppm and 0.75 cfm using 0.1N sodium hydroxide had an average collection efficiency of 90.2 percent which is in very good agreement with their reported value of 90.7 percent (the value for two similar runs using water was 74.7 percent).

TABLE 30
FLUORIDE RECOVERIES

Absorbing Reagent	Flow Rate cfm	Concentration Range ppm V/V	Number of Runs	Average Collection Efficiency	Standard Deviation	%
Distilled Water	1	10-100	5	54.4	17.6	32
	0.75	10-100	3	64.2	15.7	24
0.1N NaOH	1	10-100	5	74.0	21.1	28.5
	0.75	10-100	4	73.4	18.6	25.3

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6.0 CONTINUOUS FLUORIDE MONITOR

6.1 DESIGN

The basic design consideration for the continuous fluoride source monitor was the ability to measure gaseous and water soluble particulate fluoride compounds; the latter condition dictated that a gas scrubber be utilized in the design. The basic approach was to continuously withdraw a sample from the stack gas stream, scrub this sample with a modified Greenburg-Smith impinger and analyze the contents of this impinger using a specific ion electrode.

Figure 14 is a schematic diagram of the final design configuration. Operation of the instrument was as follows. Gas from the stack was withdrawn through the probe into the impingers where fluorides were scrubbed out with distilled water. Liquid was continuously withdrawn from the bottom of the impinger and replaced with fresh distilled water; the level of water in the impingers was controlled by an on-off type controller. Approximately 0.5 ml/min of the impinger water being drawn from the bottom was diluted with 4 ml/min of buffering reagent in a peristaltic pump. The buffering reagent had the following formula: 0.5 M sodium acetate, 0.5 M acetic acid, 0.01 M EDTA. EDTA was added to complex any heavy metal ions that would interfere with the operation of the specific ion electrode. The diluted stream was next sent to the inner chamber of the holder in which the fluoride electrode was housed. The contents of this inner chamber were kept well mixed by a magnetic stirrer. The surrounding annular space was kept filled with water at 110°F which was circulated through a Beckman sample conditioner by a separate pump to maintain this temperature; this was found to be necessary as the specific ion electrode is temperature sensitive.

A mathematical description of the system as described can be derived from a material balance over the impinger.

$$\text{Input} = \text{Output} + \text{Accumulation} \tag{1}$$

These terms are:

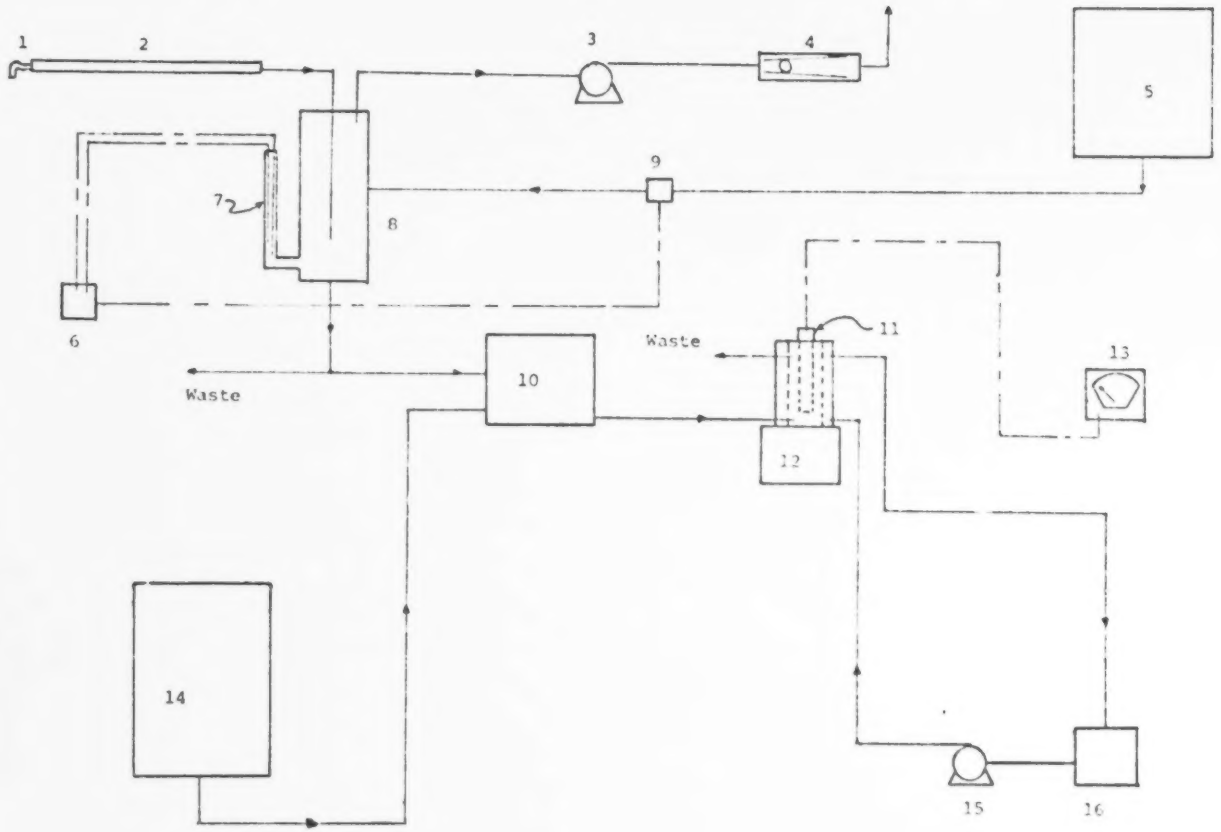
$$\text{Input} = (C_s \times 10^{-6}) \times Q_s \times \frac{492}{T} \times \frac{P}{29.92} \times \frac{20.006}{22.414} \times dt \tag{2}$$

$$\text{Output} = D \times C_L \times Q_L \times 10^{-3} \times dt \tag{3}$$

$$\text{Accumulation} = d(DVC_L) = DVdC_L \times 10^{-3} \tag{4}$$

where: C_s = stack gas concentration, ppm

Q_s = gas flow through the impingers, liter per minute (liter/min)



——— – ——— Electrical lines
——————— Fluid lines

1. Nozzle
2. Probe
3. Vacuum Pump
4. Rotometer
5. Distilled water reservoir
6. Liquid level controller
7. Liquid level probe
8. Modified Greenburg-Smith impinger
9. Solenoid valve
10. Metering pump
11. Fluoride elecytode
12. Magnetic stirrer
13. Millivolt meter
14. Buffering reagent
15. Liquid pump
16. Liquid heater

FIGURE 14

CONTINUOUS FLUORIDE MONITOR

T = gas temperature as measured through rotameter, °R

P = ambient pressure, inches Hg

20.006 = molecular weight of HF, g/mole

22.414 = molar volume at 0°C liters/9-mole

dt = time increment

D = dilution factor for liquid from impinger being mixed with buffering reagent

C_L = fluoride concentration in electrode chamber, mg/liter (ppm)

Q_L = liquid flow from impinger, liter/min

V = volume of liquid in impingers, liters

dC_L = incremental change in C_L occurring during time increment dt

Combining the above terms yields the following differential equation

$$\frac{\tau dC_L}{dt} + C_L = KC_s \tag{5}$$

where: $\tau = V/Q_L$, time constant for the system

$$K = \frac{492 \times 20.006 \times Q_s \times P \times 10^{-3}}{29.92 \times 22.414 \times D \times T \times Q_L}, \text{ a constant}$$

The solution to this equation is:

$$\frac{C_L - C_{LO}}{KC_s - C_{LO}} = 1 - e^{-t/\tau} \tag{6}$$

Where C_{LO} is the initial liquid concentration at the start of sampling ($t = 0$). The steady state solution to the above is then:

$$C_s = \frac{1}{K} \times C_L \tag{7}$$

The above equations were developed assuming that all of the fluoride in the gas stream was removed in the impinger, hence there was no output term for the gas stream. Since this assumption was made and our laboratory studies indicated that such was not the case, it was necessary to calibrate the monitor in the laboratory. The same gas dilution system that was used for the collection efficiency study was used for the calibration of the monitor. By reducing the constant factor

K, in equations 5 through 7, the following equation is derived for state operation:

$$C_s = 68.13 \frac{DQ_L T}{Q_S P} C_L \qquad (8)$$

This equation predicts a linear relationship between C_L and C_s, with a slope that will vary depending on the factor $DQ_L T/Q_S P$.

This linearity was found to be valid down to approximately 25 ppm gas concentration corresponding to 1.3 ppm liquid concentration (at this point, the impinger concentration was about 20 ppm). Below this point, the curve broke and dropped sharply. Figure 15 is the resulting curve obtained from laboratory calibration.

The quantity $\frac{DQ_L T}{Q_S P}$ was varied and essentially the same conclusion was reached: a linear relationship prevailed down to a concentration of about 25 ppm in the gas. Below this concentration, the same curve was obtained regardless of the term $DQ_L T/Q_S P$.

Statistical analysis of the data between 25 and 100 ppm gas concentration resulted in a line with a slope of 61.89 which is fairly close to the theoretical value of 68.13 from equation 8. Since laboratory calibration covered a range of from 10 to 100 ppm in the gas, it is quite possible that gases containing higher concentrations might generate a curve coinciding with equation 8. This is probably attributed to the higher scrubbing efficiency of the Greenburg-Smith impinger at higher gas concentrations (see collection efficiency study)

6.2 FIELD RESULTS

Based on the assumption that all curves will pass through the coordinates 1.3 and 25 of the curve in Figure 15, it is possible to obtain curves for different values of the parameter $DQ_L T/Q_S P$. This procedure was followed to obtain values of stack gas concentrations for field measurements made using the continuous monitor. Table 31 gives the comparative values between the monitor and concentrations as determined by the collection trains used.

Comparison between the monitor and the collection trains was quite good only at the defluorination facility where the average differences were quite small. At the DAP facility, large differences were found which can possibly be attributed to the low collection efficiency of the train at such low concentrations and the relative magnitude of errors when dealing with such low concentrations. Prior efficiency study results indicated the possibility of a collection efficiency as low as 30 percent when using a wet collection train. When this fact is considered, these results do not fare quite so poorly.

FIGURE 15

CONTINUOUS MONITOR CALIBRATION CURVE

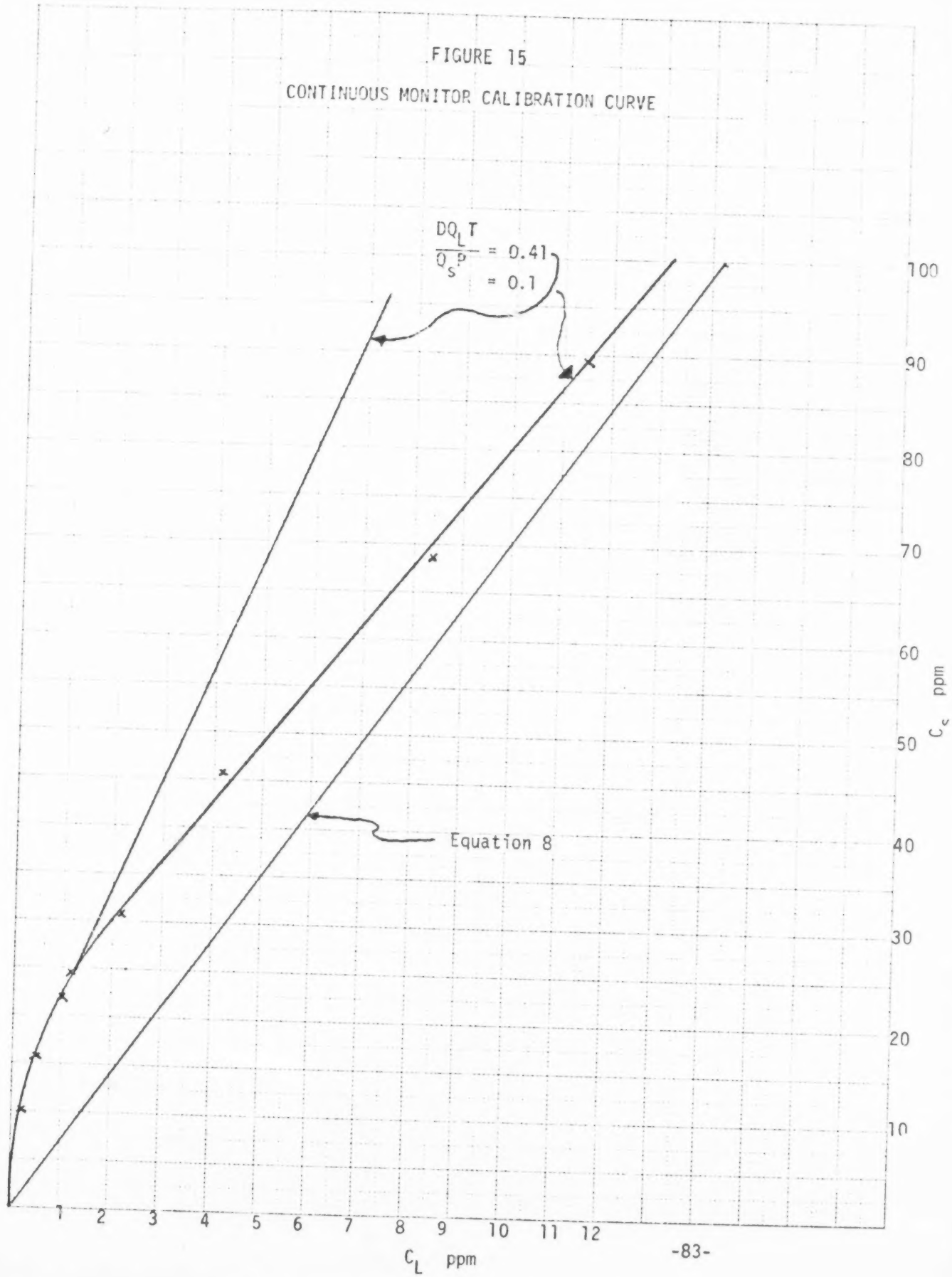


TABLE 31
CONTINUOUS MONITOR FIELD RESULTS

Operation	Date	Location	Test No.	$DQ_L T/Q_s P$	Monitor C_L (electrode ppm)	Monitor C_s (gas ppm)	Wet Collection Train
D.A.P.	1/22	Outlet	3	0.105	0.15	10	2.9
	1/24		2	0.06	0.095	7.5	1.24
	1/24		3	0.06	0.08	7	1.5
Defluorination Kiln	5/24	Outlet	1	0.14	0.34	14	14.9
	5/24		2	0.14	0.90	23	25.2
	5/25		3	0.14	9.80	99	83.2
Primary Aluminum Reduction	6/12	Inlet	1	0.17	2.90	42*	140.0
	6/13	Outlet	1	0.16	0.23	12*	15.2
	6/13		2	0.17	0.10	8*	16.4
	6/14		3	0.16	<0.05	<5*	31.0

* Erratic electrode response

At the primary aluminum reduction facility, the electrode response was very erratic which was caused by a cracked housing on the electrode.

6.3 CONCLUSIONS AND RECOMMENDATIONS

These tests, under laboratory and field conditions, have shown that the development and operation of an in-stack continuous fluoride monitor is feasible . With proper operational techniques, calibration, and recording instruments, results obtained using such a device can be comparable to those from standard wet-collection train methods.

One major problem that might be encountered could be the presence of compounds in the gas stream containing heavy metal ions that would interfere with the fluoride electrode. Although EDTA was included in the buffering solution to complex metal ions, it is possible that a gas stream might contain enough of a compound to overcome this. If this compound was in a particulate form, it could be filtered out with glass wool or some other type of filter.

Operation would, of course, be simplified if it were known that the temperature and pressure would not vary much, in which case the quantity $DQ_t T/Q_s P$ could remain essentially constant. In this case, only one calibration curve would be needed for a given source to be monitored.

APPENDIX A - TENTATIVE REFERENCE METHOD FOR SAMPLING AND ANALYZING PARTICULATE AND GASEOUS FLUORIDES FROM STATIONARY SOURCES*

1. PRINCIPLE AND APPLICABILITY

1.1 Sampling

1.1.1 Principle - Samples are collected isokinetically by apparatus which provides for the separate collection of particulate and gaseous fluorides.

1.1.2 Applicability - The method is directly applicable for analyzing "dry" streams (where "dry" refers to a relative humidity of less than 100% at stack conditions) from various industrial stationary sources, including the various processes within the primary aluminum, iron and steel, and glass industries. With only slight modification (described in Section 11), the method can be applied to analyzing "wet" streams (where "wet" refers to water or stream entrainment in the stream) such as occur for unit operations within the phosphate rock processing industry. In the latter case, particulate and gaseous fluorides cannot be separated.

1.2 Analysis

1.2.1 Principle - Fluoride ion in the collected sample is measured with the fluoride specific ion electrode. If the sample to be analyzed contains particulate, a caustic fusion must be performed to ensure that all fluoride will be soluble. A distillation of the sample from sulfuric acid prior to the electrode measurement is required for removal of interfering ions.

1.2.2 Applicability - The method as written is applicable to any type of sample collected from process effluents which are discharged into the air from unit processes within the primary aluminum, iron and steel, glass and ceramic, and phosphate rock industries. The nature of the sample collected has little effect on the success of the analysis, so that the procedure should be generally applicable to stationary source fluoride emissions from other industries.

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*This method is based on laboratory evaluations, discussions with industrial representatives and reference to the open literature. The method cannot be accepted as final until suitable field tests have been conducted and modifications to the method are made, as appropriate.

2. RANGE AND SENSITIVITY

2.1 Sampling - Not Available

2.2 Analysis - The fluoride electrode can measure fluoride concentrations in the range of 0.02-2,000 µg/ml; however, measurements of less than 0.2 µg/ml require a great deal of care and should be avoided. Since the electrode measurement is performed on an aliquot of 50- ml of solution containing the sample, the practical lower limit = 100 µg of fluoride; the reagent blank for fusion and distillation averages 10 µg fluoride. The upper limit of fluoride which can be measured has not been determined with certainty; 20 mg has been measured successfully.

3. INTERFERENCES

3.1 Sampling - Although evaluations are incomplete, there may be an interference from the materials of construction of the sample train components which could influence the fluoride recovery by the sampling system. Also, physical and chemical absorption of gaseous fluorides onto particulate can effect the apparent gaseous to solid fluoride distribution.

3.2 Analysis - The presence of more than the 1 mmole of silicon or iron, or more than 10 mmoles of aluminum can retard the evolution of fluoride during distillation. Large amounts of lead can have a similar effect. The maximum amount of metal which can be tolerated depends to some extent on the amount of fluoride in the sample. Maximum upper limits remain to be determined.

4. PRECISION, ACCURACY, AND STABILITY

4.1 Sampling

4.1.1 Precision - Not Available

4.1.2 Accuracy - Not Available

4.1.3 Stability - Based on limited data, it appears that the particulate catch, probe washings, and impinger solutions remain stable and unchanged for at least a month as long as they are stored in sealed polyethylene or flint glass containers.

4.2 Analysis - Reliable estimates of precision, accuracy, and stability when analyzing field samples are not yet available. Although very tentative, some estimates drawn from laboratory studies are presented below.

4.2.1 Precision - At the 2 mg fluoride level, a relative standard deviation of ± 2% or better was achieved on sets of quadruplicate samples.

4.2.2 Accuracy - Accuracy depends first upon the accuracy with which the fluoride content of the standardization samples is known. The more important limitation on accuracy is the effect of metals (see 3.2) on distillation recovery. Within the constraints of 3.2, 95% or better recovery can be achieved.

4.2.3 Stability - The one source of instability in the method is potential drift in the electrode response. A calibration curve, if used, should be generated daily and a known, mid-range standard should be measured as a check at least once per hour. If direct readout is employed, the span should be checked hourly.

Electrode response is temperature sensitive; relative concentration indicated will change about 1.5% relative/°C. If ambient lab temperature fluctuates more than a few degrees, it is advisable to place samples in a water bath prior to measurement. If an electrically-driven magnetic stirrer is used, precaution should be taken to see that it does not heat the solution.

5. APPARATUS

5.1 Sampling

5.1.1 Sample Probe - A 5-foot (or longer) length by 1/2 to 5/8 inch diameter 3.6 stainless steel with appropriate nozzle and orifice;

or

A 5-foot length by 1/2 to 5/8 inch diameter borosilicate glass tubing encased in a metal support tube fitted with an appropriate stainless steel nozzle and orifice, with provision for heating the probe to maintain a gas temperature of 250°F.

5.1.2 Particulate Collector - A 316 stainless steel or Pyrex filter holder with suitable filter media (glass fiber, organic membrane, or paper) of high collection efficiency, which may be preceded by a 316 steel or Pyrex cyclone;

A stainless steel enclosed electrostatic precipitator as described in Reference A-1; both systems including a heating system capable of maintaining any temperature up to 250°F.

5.1.3 Impingers - Two, 500 ml Greenburg-Smith impingers made from polyethylene or glass and containing 200 ml of distilled water or 0.1N NaOH, to be contained in an ice bath.

5.1.4 Mist Trap - A 500 ml bottle containing a suitable desiccant (such as 175g of dried silica gels) for protection of down stream components from moisture.

5.1.5 Vacuum Pump - Rates at 4 cfm at 0 in.Hg and 0 cfm at 26 in.Hg.

5.1.6 Dry Gas Meter - Rates at a maximum of 175 cm. ft. per hour.

5.1.7 Air Flowmeter - a calibrated rotameter or critical orifice capable of measuring airflow within 2%.

5.2 Analysis

5.2.1 Fusion Crucible - Crucible, nickel or Inconel, 60 ml capacity.

5.2.2 Distillation Assembly - Glassware (shown in Figure A-1) consisting of a 1-liter, round bottom, borosilicate boiling flask (b), an adapter with a thermometer opening (c), a condenser (f), and a thermometer reading to 250°C(d). Standard taper or spherical ground-glass joints shall be used throughout.

Heat is provided by a hemispherical heating mantle (a) connected to a laboratory variable transformer. Distillate is collected in a 500 ml volumetric flask(g).

5.2.3 Fluoride Specific Ion Electrode System

5.2.3.1 Fluoride Ion Specific Electrode (Orion Model 94-09 or equivalent)

5.2.3.2 Reference Electrode - Silver/silver chloride or saturated Calomel suitable for use with the fluoride electrode and electrometer used. A large area liquid junction is preferable to a fiber-type liquid junction.

5.2.3.3 Electrometer - (more commonly a pH meter with millivolt scale, or a "Specific Ion Meter" made specifically for ion-specific electrode use) capable of ± 0.5 mv. resolution.

6. REAGENTS

6.1 Sampling

6.1.1 Distilled Water

6.1.2 0.1N NaOH (optional)

6.2 Analysis

6.2.1 Fusion Flux - Either NaOH or Na_2CO_3/K_2CO_3 (equimolar mixture) may be used and should be as low in fluoride as possible.

6.2.2 Calcium Oxide - low-fluoride, can be obtained commercially or can be prepared from pure calcium metal.

6.2.3 Concentrated Sulfuric Acid - reagent grade.

6.2.3 Citrate Buffer - 1.0 M stock solution. Dissolve 294.1 g of reagent grade $Na_3C_6H_5O_7 \cdot 2H_2O$ in 1 liter of distilled water.

6.2.5 Fluoride Standard Solution - A 0.1M fluoride standard solution is commercially available, or it can be prepared by dissolving reagent grade sodium fluoride in water.

7. PROCEDURE

7.1 Sampling

7.1.1 Prior to sampling, measure stack gas velocity at a series of test points to determine the velocity profile of the stack, using procedures such as those given in Reference A2. If variation is 10% or less, sampling may be carried out at point of average velocity. If variation exceeds 10%, sampling must be carried out incrementally at a series of test points to reflect an average velocity.

7.1.2 Sampling will be isokinetic at a rate between 0.75 and 1.25 cfm.

7.1.3 Sampling time will reflect all cyclic variations in the process being monitored, but will not be less than 60 minutes.

7.1.4 After completion of sampling, the train shall be disassembled and the collected materials placed in containers. The final volume of the impinger catch will be noted to calculate moisture content of the gas. Separate containers will be used for the particulate catch, impinger catch and washings, and probe washings.

7.2 Analysis

7.2.1 Preparation of Sample for Distillation - Whether the fluoride samples have been collected by an electrostatic precipitator in NaOH solutions, or on filters, they generally require some treatment before a distillation can be made. Organic matter must be destroyed without incurring any fluoride losses, and large volumes of solution must be evaporated to volumes which will permit their placement in the distilling flasks. Several precautions are mandatory when preparing samples for distillation.

7.2.1.1 Filter Paper Sample - Fold the filter paper with the clean side out and place in a nickel or Inconel crucible. Saturate the paper with slurry of lime water prepared from fluoride-free CaO. Complete saturation of the paper is essential to prevent loss of fluoride. Heat the crucible and contents on a hot plate to remove excess water. When dry, ash the sample in a muffle furnace at a temperature not in excess of 600°C until no carbon remains. Ordinarily this is accomplished in less than 1 hr. Remove the crucible from the furnace, cool, and add 3 g of NaOH (or 4.5 mixed carbonates). Fuse the contents over a burner for ten minutes, and then allow to cool.

7.2.1.2 Molecular Filter Sample - Proceed in accordance with 7.2.1.1 for filter papers, except to omit folding, and thoroughly char the filter on the hot plate at low hear, prior to ignition. Excessive heat causes an instantaneous ignition of the filter with an attendant loss of sample.

7.2.1.3 Impinger Sample - If the impinger sample contains insoluble particulate, transfer it to a nickel or Inconel beaker, add 0.1 g CaO and 3 g of NaOH, and evaporate to dryness. Fuse over a burner for 10 minutes and allow to cool.

Alternatively, the slurry can be filtered and the filter paper and solids treated as in 7.2.1.1 and the clear filtrate as follows.

If the impinger sample contains no undissolved solids, it is ready for distillation. If the sample volume is greater than 300 ml, a 300 ml aliquot can be taken for distillation, or if the fluoride level is low, the volume can be reduced by boiling after adding 0.1 g CaO.

7.2.1.4 Electrostatic Precipitator Sample - Wash the contents of the precipitator into a 250 ml nickel or Inconel beaker with water. Add 0.1 g CaO and 3 g of NaOH, evaporate to dryness, and fuse over a burner for 10 minutes. Allow the fusion to cool prior to distillation.

7.2.2 Distillation

7.2.2.1 Charging the Flask with Acid - Place 400 ml of water in the distilling flask and add 200 ml of concentrated H_2SO_4 (sp gr 1.84). Observe the usual precautions while mixing the H_2SO_4 by slow addition of the acid accompanied by constant swirling. Add sufficient boiling stones and assemble the apparatus. Heat the solution in the flask, preferably with an electric heating mantle, until the temperature of contents reaches exactly 210°C. A quartz heating mantle is preferred in order to reach the required 210°C in a minimum time. The tip of the thermometer must extend below the level of the liquid in the flask at this point. Discard the distillate. The procedure, to this point, serves to adjust the acid-water ratio for subsequent distillations. Before proceeding to add the sample, cool to a temperature of less than 60°C. (See Figure A-1).

7.2.2.2 Distillation - The sample in a total liquid volume of 300 ml is then slowly transferred to the flask, with good mixing by swirling, for distillation. Solid samples from fusions can be broken up with a spatula and the fine chunks introduced directly with the aid of a water wash. Additional water should then be added so that the total water added is about 300 ml. In this case, the exact volume is not critical. With clear impinger solution, an aliquot ≤ 300 ml whose volume is accurately known must be used. If the aliquot is < 300 ml, additional water should be added.

The flask is then heated and distillate collected until the temperature again reaches exactly 210°C. Step 7.2.2.2 may be repeated with the same acid charge for 2 or 3 additional sample distillations.

7.2.3 Analysis

7.2.3.1 Calibration - Fluoride standards are prepared by taking aliquots of the 0.1 M stock solution, adding 5.0 ml of 1 M citrate buffer, and diluting to a final volume of 50 ml. For wide dynamic range measurements, seven standards spanning the range 10^{-2} - 10^{-6} M are adequate. The standards are measured and a calibration curve (millivolts vs. log concentration) is constructed.

For measurements over a narrower range, certain meters may be calibrated to read directly in ppm fluoride by calibration with two known solutions.

7.2.3.2 Measurement - The collected distillate is diluted to 500 ml and a 25 ml aliquot is pipetted into a 50-ml volumetric flask. Four drops of bromthymol blue are added and, if necessary, pH adjusted to be in the range of 6.6 - 7.1 (indicator is green in color). Five milliliters of 1.0 M citrate buffer is added, and the resulting solution diluted to 50 ml.

The solution is transferred into a beaker, the fluoride electrode immersed and the EMF in millivolts (or ppm F if instrument is direct reading) is read. Concentration of fluoride is read from the calibration curve.

8. CALIBRATION, STANDARDS, AND EFFICIENCIES

8.1 Sampling - Not Available

8.2 Analysis - The electrode measurement is calibrated daily and checked hourly. Fusion and distillation are not normally calibrated but assumed to be quantitative. Tests to date indicate that this assumption is valid, but field testing is required to substantiate it. The entire method should be run occasionally at appropriate time using a primary standard such as NaF, cryolite, phosphate rock, etc. to ensure that it is indeed working properly in a particular laboratory for a particular analyst.

9. CALCULATIONS

9.1 Sampling - From measurements of gas temperature, barometric pressure and collected volume of water, calculate dry gas volume and total gas volume at standard conditions. These volumes are required for subsequent calculations of fluoride concentration.

9.2 Analysis - Total mg F in the submitted sample is computed from the mg/liter value derived from the calibration curve as follows:

$$\text{milligrams F} = (\text{mg/ml}) \times 1000 \times \frac{\text{total sample volume}}{\text{volume of sample taken}}$$

10. REFERENCES

10.1 Sampling

A1 G. L. Rounds and H. J. Matoi, "Electrostatic Sampler for Dust-Laden Gases", Anal. Chem. 27, 1955, 829-830.

A2 "Standards of Performance for New Stationary Sources", Federal Register 36, August 17, 1971, 15704-15722.

10.2 Analysis

A3 ASTM Method D1606-60 "Standard Method of Test for Inorganic Fluoride in the Atmosphere."

A4 ASTM Method D1179-68, "Standard Method of Test for Fluoride Ion in Industrial Water and Industrial Waste Water."

11. MODIFICATION FOR MEASUREMENT OF WET GAS STREAMS

The procedure for measuring fluorides in wet gas stream is the same as above, except for the following modifications:

5.1.2 Delete

7.1.4 Change third sentence to: The impinger catch and washings and the probe washings will be combined and placed in one container.

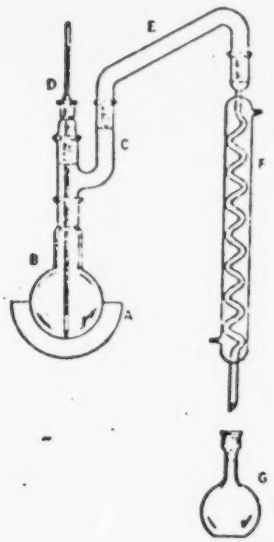

Figure A-1 Distillation Assembly for Fluoride Isolation

A. Heating Mantle (quartz).

B. Round-bottom Flask, 1000 ml.

C. Adapter with thermometer opening.

D. Thermometer 250°C.

E. Connecting tube.

F. Graham condenser, 300 mm.

G. Volumetric flask - 500 ml.

DETERMINATION OF FLUORIDES IN STACK GAS: SPADNS - ZIRCONIUM LAKE METHOD

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DETERMINATION OF FLUORIDES IN STACK GAS:

SPADNS - ZIRCONIUM LAKE METHOD

INTRODUCTION

This method is intended for the determination of gaseous and particulate fluorides in stack gas samples. Particulate and gaseous fluorides are collected from the same stack gas sample using a combination particulate - gas sampling train, consisting of probe, cyclone, filter, and Greenburg-Smith impingers containing distilled water. Particulate fluorides are collected using a high-efficiency cyclone followed by a Whatman No. 41 filter. Gaseous fluorides in the stack gas react with a hot glass probe to form gaseous silicon tetrafluoride, which hydrolyzes in water to form soluble fluosilicic acid and slightly soluble orthosilicic acid, and are collected in the Greenburg-Smith impingers. Water-soluble particulate fluorides, total particulate fluorides, and soluble gaseous fluorides are determined separately. Interfering substances are eliminated by distillation of the fluosilicic acid from sulfuric acid.[1] Chloride interference is eliminated, if present, by additon of Ag_2SO_4 to the distillation mixture. Fluorides recovered in the distillate are determined spectrophotometrically at 570 mu by the bleaching reaction of fluoride in a zirconium-dye lake. (Spadns Method).[2] Fluoride ions combine with zirconium in the red-colored lake to form colorless $(Zr\ Cl_6)^{-2}$ and the colorless form of the azo dye. Beers' law is obeyed in the fluoride concentration range of 0 - 1.4 µg/ml.

REAGENTS

All chemicals used must be ACS analytical reagent grade.

Spadns Solution Dissolve 0.959 gram of 4,5 - dihydroxy - 3 (p-sulfophenylazo) - 2,7 - napthalene disulfonic acid, trisodium salt (Spadns), at room temperature, if protected from sunlight.[3]

Zirconyl Chloride Octahydrate Solution Dissolve 0.133 gram of $ZrOCl_2 \cdot 8H_2O$ in 25 ml of H_2O. Add 350 ml of concentrated HCl, and dilute to 500 ml with distilled water. This solution is stable at room temperature for at least 3 months.

Spadns Reagent Combine equal parts of the Spadns solution and $ZrOCl_2 \cdot 8H_2O$ solution, and mix thoroughly. This reagent is stable for at least 2 years.[3]

Reference Solution Dilute 7 ml of concentrated HCl to 10 ml with distilled H_2O. Add 10 ml of Spadns solution to 100 ml of distilled water and add the HCl solution. Mix well. This solution is used to set the spectrophotometer zero point and is stable indefinitely.[3]

Standard Fluoride Solution Dissolve 2.2105 grams of dry NaF, and dilute to 1 liter with distilled water. Dilute 1 ml of this solution to 1 liter. This final solution contains 1.0 mg/ml of fluoride.

APPARATUS

Sampling Apparatus The sampling apparatus consists of probe, cyclone, filter, four impingers, flowmeter, manometer, dry meter, and air pump. The numbers in parentheses indicate number shown on Figure 1. The stainless steel, button-hook type probe tip (1) is drawn to 5/8 inches so that it will

connect by a stainless steel coupling (2) with Viton "O" ring bushings to the probe (3). The probe (3) consist of 5/8 inch medium wall Pyrex glass tube with 28/12 $\frac{T}{S}$ ball joint on one end. The glass probe is wound with 25 feet of 26-gauge nickel-chromium wire. During sampling, this wire is connected to a transformer. The wire-wound glass tube is wrapped with a fiber glass tape and encased in a 1-inch stainless steel tube. The end of the tube that does not have the ball joint protruding has a nut welded to it for connection to the stainless steel coupling. The probe connects to a cyclone and flask (4). The cyclone is described in detail in Reference 5 except for the 28/12 female ball joint on the arm. The cyclone is designed to trap particles larger than 5 microns in diameter. The cyclone connects to a fritted glass filter (5), which holds a 2-1/2-in. No. 41 Whatman filter paper. The cyclone, flask, and filter are contained in an electrically heated enclosed box (6), which is thermostatically maintained at 250° F. Attached to the heated box is an ice bath (7) containing four impingers connected in series. The first impinger (8) receives the stack effluent from the filter. The impinger is of the Greenburg-Smith design modified by replacing the tip with a 1/2-in. ID glass tube extending to 0.5 in. from the flask bottom. This impinger is filled with 250 ml of distilled water. The second impinger (9) is a normal Greenburg-Smith impinger filled with 150 ml of distilled water. The third impinger (10) is identical to the first. This impinger is left dry. The fourth impinger (11) is also identical to the first. This impinger contains approximately 175 grams of accurately weighed dry silica gel. From the fourth impinger (11), the effluent stream

flows through: a check valve (13); flexible rubber vacuum tubing (14); a needle valve (16); a vacuum pump (17), rated at 4 cubic feet per minute at 0 in. of mercury gauge pressure, and in parallel with a by-pass valve (18); a dry test gas meter (19), 1 cubic foot per revolution. The three thermometers (12) are dial type with a range from 25° to 125° F and have a 5-in. stem. The vacuum gauge (15) is calibrated between 0 and 30 in. of mercury. The manometers (21) across the calibrated orifice (20) and pitotmeter (22) are the inclined-vertical type graduated in hundreths of an inch of water from 0 to 1.0 in. and in tenths from 1 to 10 in.

Distillation Apparatus All-glass distillation apparatus as shown in Figure 2 consists of a boiling flask, thermometer, connecting tube, condenser, and receiver. The distillation thermometer should be capable of measuring temperature in the range from 30° to 200° C with an accuracy of ±1° C. An automatic distillation unit with thermo-regulated shut down may also be used.[4]

Gas Burner A Meker type burner is used.

Pipettes Volumetric pipettes of the following sizes are needed: 1, 5, 10, 25, 50, and 100 ml.

Spectrophotometer This instrument should be capable of measuring color intensity at 570 mμ in 0.5-in. aborbance cells.

ANALYTICAL PROCEDURE

Collection of Samples Sampling is performed isokinetically along a representative traverse of stack. Assemble the equipment as indicated in Figure 1 and as described on Page 2. The heated box and ice bath

with their respective glassware move with the probe. Keep the probe sufficiently hot so as to avoid condensation. Place the remainder of the equipment at some convenient location, and connect by the rubber vacuum hose. Select a probe tip so that isokinetic sampling will be obtained at approximately 0.75 cubic foot per minute. Adjust the sampling rate to isokinetic by the needle valve (16) and by-pass valve (18). Determine the gas sampling rate at any instant from the inclined-vertical manometer (21) connected across the calibrated orifice. Convert the dry gas sampling rate to total gas sampling rate by correcting for the moisture condensed and absorbed out of the stack effluent by the impingers. Generally, other condensable or soluble gases, including fluorine, are not a significant part of the gas volume sampled from most stacks; and they need not be considered. If the moisture content of the stack effluent is not known, determine same from a preliminary nonisokinetic test of the stack effluent. The moisture content is determined from the water condensed and absorbed by the impingers for a given volume of dry gas sampled. Use the thermometer after the fourth impinger to indicate ice bath efficiency. Sample at each traverse point so that the total sampling time is at least 40 min. Determine the gas volume sampled at each point from the dry test gas meter (19). Obtain the temperature at which the dry gas was measured by averaging the temperatures indicated by the thermometers before and after the dry gas test meter.

When sampling is completed, measure the volume of the contents of the first three impingers and quantitatively wash the contents with deionized

water into a sample bottle. Determine the moisture content of the sampled gas from the initial 400 ml of water present, plus the volume of water absorbed by the silica gel. Quantitatively wash with acetone the contents of the probe and cyclone into a second sample bottle. Remove the filter from the filter holder. Quantitatively wash with acetone the contents of the filter holder into a third sample bottle. Insert the filter into a plastic sample weighing bottle.

Sample Preparation Sample preparatory procedures are as follows:

1. Impinger Solution (approximate volume 400 ml). Transfer the sample to a 1-liter graduated cylinder, and adjust to the 1-liter mark with distilled water.

2. Particulate Samples.

   a. Transfer cyclone and probe washings quantitatively to a tared 150-ml beaker with acetone, and evaporate to dryness. Dry at 110° C for 2 hrs in an oven; desiccate and weigh on an analytical balance to the nearest 0.1 mg. Record net weight of particulate.

   b. Transfer the filter sample particulate to a glass weighing dish and dry in an oven at 110° C for 2 hours. Transfer to a desiccator; cool and weigh to the nearest 0.1 mg. Continue the drying process at 110° C until the filter and particulate come to a constant weight. Record the net weight of the filter particulate.

c. Transfer filter holder washings to a tared beaker with acetone and evaporate to dryness. Dry at 110° C for 2 hrs in an oven, desiccate and weigh to the nearest 0.1 mg. Record net weight of the particulate.

3. Transfer all particulate samples (a, b, c) to a 250-ml graduated glass-stoppered cylinder, and dilute to 250 ml with distilled water. The filter is shredded with the aid of forceps before transfer. Mix well, and transfer the total contents of the graduated cylinder to a 300-ml Erlenmeyer flask.

4. To estimate the appropriate aliquot size to be used in the distillation procedure, take a 25-ml aliquot of each type of sample (impinger, water soluble particulate, total particulate) and apply the spectrophotometric procedure. From the amount of fluoride found in the undistilled aliquot, calculate the sample aliquot needed to yield 0.5 to 0.9 mg of fluoride, preferably closer to 0.5 mg.

Distillation Procedure

Place 400 ml H_2O, 200 ml concentrated H_2SO_4, and about 25 carborundum chips into the boiling flask, and swirl to mix. Caution - the sulfuric acid-water solution should be mixed thoroughly before heat is applied to prevent splattering. Connect the apparatus as shown in Figure 2. Begin heating slowly at first, then rapidly until a temperature of 180° C has been reached.[2] The connection between the boiling flask and condenser

must be separated immediately after the heat is removed to prevent suck-back of the sample and for safety reasons. About 300 ml of water should have been distilled over in about 45 minutes. At this point, the apparatus has been flushed free of fluoride and the acid-H_2O ratio has been adjusted. When the flask has cooled to 120° C, the apparatus is ready for the sample.

Add 300 ml of distilled water containing an aliquot of the impinger sample corresponding to 0.5 to 0.9 mg of fluoride to the boiling flask; swirl to mix; and connect the apparatus and distill as before until the distillation temperature reaches 180° C. For distillation of water-soluble particulate fluorides, take a suitable aliquot of the supernatant liquid of the particulate sample, dilute to 300 ml with distilled water, and add to the distillation flask. For distillation of total particulate fluorides, use a suitable aliquot of the water-soluble plus water-insoluble sample. To obtain a representative sample, withdraw an aliquot using a calibrated, sawed-off pipette, immediately after intimate mixing of the sample. In no case should the aliquot contain more than 0.9 mg of fluoride. Distill the sample, as before, until a temperature of 180° C has been reached. Fluoride content of phosphate rock or fertilizer may be determined using these same procedures, provided the approximate percent weight of fluoride in the sample is known so that the still is not overcharged Weigh out a sample to the nearest 0.1 mg, corresponding to about 0.5 mg of fluoride, dilute to 300 ml with distilled water and distill as before until a temperature of 180° C has been reached. Pipet a suitable aliquot (containing 10 to 40 µg of fluoride) from the distillate and dilute to 50 ml.

Add 10 ml of Spadns reagent, mix thoroughly, and read the absorbance. If the absorbance falls beyond the calibration curve range, repeat the procedure using a smaller aliquot.

CALCULATIONS

$$X = \frac{44.82\ (C)\ (F)}{V_S}$$

where:

C = concentration fluoride in aliquot, mg

F = dilution factor

V_S = volume of gas sample at 70° F and 29.92 inches Hg, scf

X = ppm fluoride

$$44.82 = \frac{\frac{530^\circ F}{492^\circ F} \times 22.4 \frac{\text{liters}}{\text{mole}} \times 10^6}{19 \frac{g}{\text{mole}} \times 10^3 \frac{\text{mg}}{g} \times 28.32 \frac{\text{liters}}{\text{cu ft}}}$$

PREPARATION OF CALIBRATION CURVE

570 mμ

Pipet exactly 0.0, 10.0, 20.0, 30.0, 40, and 50.0 ml of standard NaF solution into separate 100-ml beakers. Add 50.0, 40.0, 30.0, 20.0, 10.0, and 0.0 ml of distilled H_2O respectively, to the beakers. Add 10 ml of Spadns reagent to each beaker. Mix thoroughly, and let stand for 15 min. at room temperature. Determine the absorptivity of the reference solution. The absorptivity of the reference solution should be in the range of 0.82 to 0.85. Then, set the instrument to zero absorbance using the reference solution.

Plot concentration versus absorbance on rectilinear graph paper.

Rerun a new calibration curve each time a new batch of Spadns reagent is prepared. It is important that standards and samples be at the sample temperature because each degree difference causes about 0.01 mg/liter error.

DISCUSSION OF PROCEDURE

The estimated error for the combined sampling and analytical procedure is ± 15 percent. The error of the analytical method is ± 4 percent. The spectrophotometric measurements should be reported to the nearest 0.5 µg. Aluminum, calcium, chloride, ferric, managanese, magnesium, phosphate, and sulfate ions interfere positively in the Spadns method.[1] These interferences are removed during the distillation of the sample. Chloride interference can be eliminated when present in high concentrations by the addition of 5 mg silver sulfate per mg of chloride. Addition of a few crystals of Ag_2SO_4 to a small portion of the sample should be performed before distillation to determine if chloride ions are present.

The determination of fluorides using this procedure may be carried out at any temperature within the range of 15° to 30° C. The important consideration here is that standards and sample should be at nearly identical temperature, because an error of 0.01 mg/liter of fluoride is caused by each degree difference in temperature.[2] Color stability after the initial 15-min. period is about 2 hrs.

When the fluoride content of the aliquot is above 0.9 mg, the distillation apparatus should be purged with 300 ml of distilled water so that no residual

fluoride is carried over when the next sample is distilled. Keeping the fluoride content around 0.5 mg eliminates the necessity of purging the distillation apparatus between samples. The acid need not be replaced until the accumulation of ions causes carryover of interferences or retards fluoride recovery. An occasional recovery check with standard fluoride samples will indicate when the acid is to be replaced.[1]

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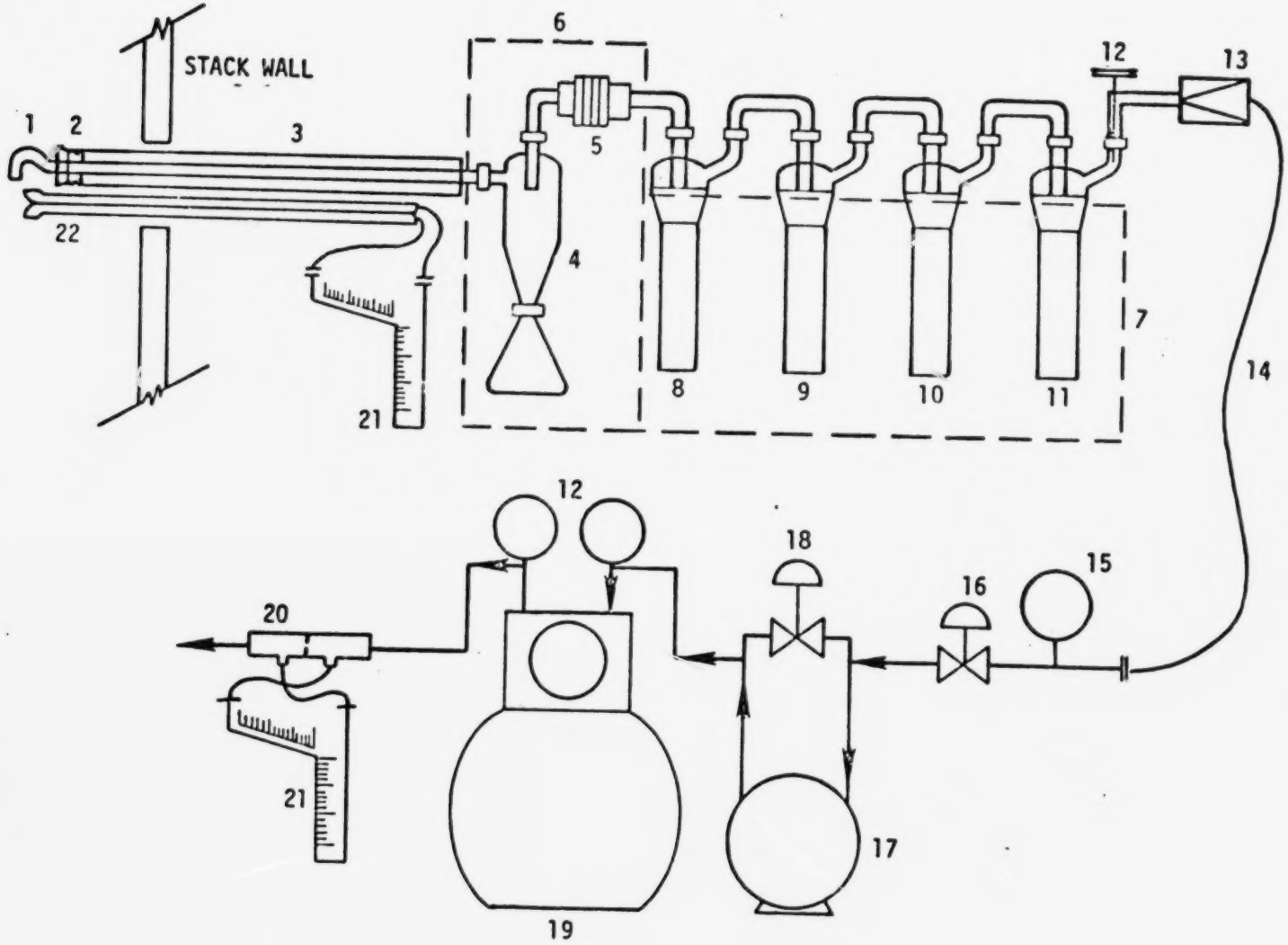

Figure 1. Particulate sampling train.

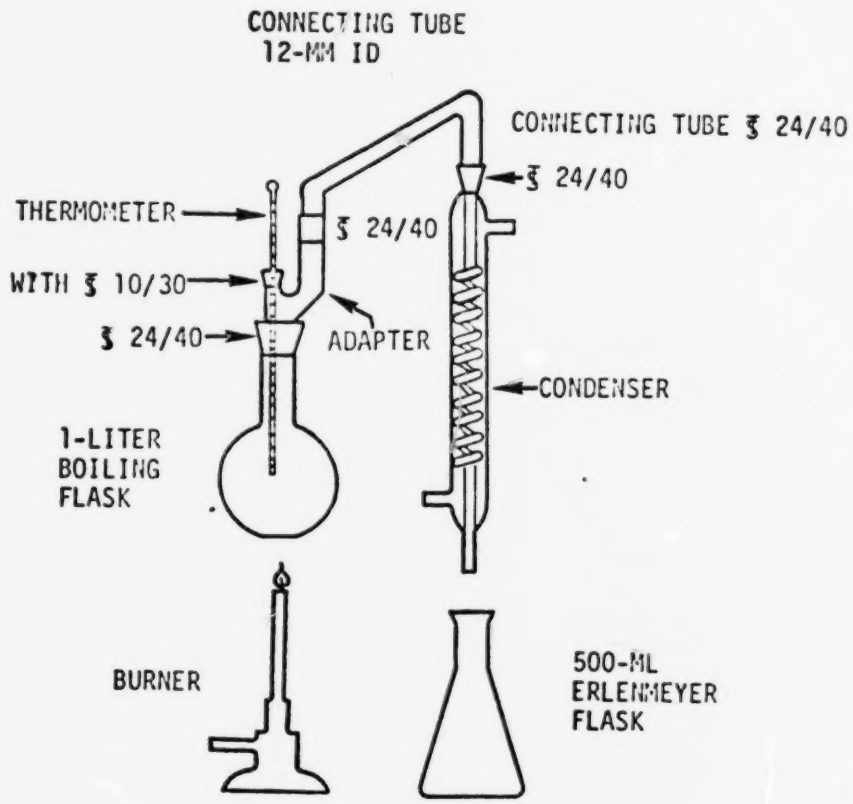

Figure 2. Fluoride distillation apparatus.

TENTATIVE METHOD OF ANALYSIS FOR FLUORIDE CONTENT OF THE ATMOSPHERE AND PLANT TISSUES (MANUAL METHODS)

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PART A: *Introduction (General Precautions and Sample Preparation)*

PART B: *Isolation of Fluoride (Willard-Winter Distillation)*

PART C: *Isolation of Fluoride (Ion Exchange)*

PART D: *Isolation of Fluoride (Diffusion)*

PART E: *Determination of Fluoride (Titrimetric Method)*

PART F: *Determination of Fluoride (Spectrophotometric Method)*

C-3

PART A: Introduction (General Precautions and Sample Preparation)

1. General Precautions

1.1 Fluorine is one of the more common elements and occurs in at least trace amts in virtually all natural and manufactured materials. Contamination by extraneous fluoride may, therefore, come from such sources as sampling and laboratory apparatus, reagents, and from exposure to laboratory dust and fume. Care must be exercised in the selection, purification and testing of reagents and apparatus, and only minimal exposures of samples should be permitted.

1.2 Vessels used for evaporation, ashing, or caustic fusion of samples are first rinsed with warm, dilute acid (hydrochloric or nitric) solution, then with distilled water and air dried under clean toweling. Inconel crucibles used for fusion of ash may require additional cleaning by boiling in 10 per cent (w/v) NaOH for one hr. Glassware is washed with hot detergent solution followed by a rinse in warm, dilute acid; it is finally rinsed with distilled water and dried (see Footnote 3 on the cleaning of distilling flasks). All sampling devices, containers, volumetric glassware, reagent solutions, etc. are stored under suitable conditions of protection from airborne dusts and fumes, and are reserved for exclusive use in fluoride analysis.

1.3 Before proceeding with analysis of samples, blank determinations are repeated until satisfactorily low values (5 μg. or less, total fluoride per determination) are consistently obtained. Calibration standards are analyzed whenever new batches of reagent solutions are prepared. In addition, one blank and one standard determination are carried through the entire analyte procedure with each set of 10 or fewer samples. If samples are handled in larger sets, the ratio of one blank and one standard per 10 samples should be maintained.

2. Sample Preparation

2.1 The techniques of sample recovery and preparation will vary, as described below, with the sampling method and equipment and will also depend upon the procedures selected for isolation and measurement of fluoride. Until proof to the contrary is established, samples are assumed to contain fluoride in refractory forms in addition to the commonly encountered interfering materials. Many details involved in the determination of gaseous and particulate fluorides in the atmosphere and in vegetation are discussed by Pack, et al. (13) * and automatic apparatus for the determination of ambient atmospheric hydrogen fluoride content down to 0.1 ppb has also been described (21).

2.2 Particulate Fluorides

2.2.1 Particulate matter collected in air sampling generally requires fusion with sodium hydroxide for conversion into soluble form prior to separation of fluoride by Willard-Winter distillation (22). This treatment is also necessary for materials containing fluoride associated with aluminum, for materials high in silica, and for many minerals.

2.2.2 Transfer the sample-bearing paper filter to a resistant crucible, e.g. platinum, nickel, or Inconel, moisten with water and make alkaline to phenolphthalein with special low-fluoride calcium oxide.† After evaporation to dryness, ignite the paper in a muffle furnace at a temp of 550–600 C until all carbonaceous material has been oxidized. Control combustion of filters of the membrane cellulose ester type by drenching with ethanolic sodium hydroxide and igniting with a small gas flame.

2.2.3 Remove particulate matter, collected by electrostatic precipitation, from the surfaces of both electrodes with the aid of a rubber policeman and distilled water. Make the resulting suspension alkaline and evaporate to dryness.

2.2.4 Integrated samples in those containing both gaseous and particulate fluorides, which have been collected on glass fiber filters, are not amenable to fusion. Filters are transferred directly to the distillation flask. Integrated samples collected in impingers are transferred to beakers made of nickel, platinum, or other resistant materials, evaporated to dryness in the alkaline condition and the residue ashed if organic matter is present.

2.2.5 Fuse the impinger sample residue from ashing of a filter, or electrostatic precipitator catch, with 2 g of sodium hydroxide. Dissolve the cold melt in a few ml of water, add a few drops of 30 per cent hydrogen peroxide to oxidize sulfites to sulfates and boil the solution to destroy excess peroxide. The sample solution is then ready for isolation of fluoride.

2.3 Gaseous Fluorides

2.3.1 Dry Collectors

2.3.1.1 Treat filter papers impregnated with calcium-based fixative agents as described above for particulate fluorides, except that caustic fusion of the ashed residue is not required.

2.3.1.2 Filters impregnated with soluble alkalies are leached with water, as are fixative-coated beads or tubes. Evaporate the washings on a suitable vessel and maintain in an alkaline condition during reduction to a volume con-

* The bold face numbers in parentheses refer to the list of references appended to this method.

† Available on special order from G. Frederick Smith Chemical Co., P.O. Box 2047, Columbus, Ohio 43223.

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venient for the subsequent fluoride separation procedure. Add a few drops of 30 per cent hydrogen peroxide and boil the solution to destroy excess peroxide.

2.3.1.2 Gaseous fluorides collected on glass fiber filters cannot be quantitatively removed by leaching with water. Transfer such filters directly to the flasks in which a Willard-Winter distillation is to be conducted.

2.3.2 Wet Collectors

2.3.2.1 Transfer a sample collected in water or alkaline solution to a suitably sized vessel, make alkaline to phenolphthalein with sodium hydroxide, and evaporate to the desired volume. Treat the solution with 30 per cent hydrogen peroxide and destroy the excess peroxide by boiling before proceeding with the isolation and determination of fluoride.

2.4 *Vegetation*

2.4.1 Reduce the gross specimen to manageable size for mixing by use of hand shears or, in the case of dried materials, a Wiley cutting mill. Take a small portion (10 to 25 g) of the mixed specimen for determination of moisture by oven drying at 80° C for 24 to 48 hr.

2.4.2 Adjust the wt of material taken for fluoride determination according to condition of the specimen: 100 to 150 g of fresh or frozen vegetation is satisfactory, while for dried materials, such as cured hay, dried leaves, straw, etc., a 50 g portion is adequate.

2.4.4 Weigh the sample into a resistant vessel,[9] make alkaline to phenolphthalein by addition of low fluoride calcium oxide slurry, and maintain alkalinity during evaporation to dryness on a hot plate. Raise the temp of the hot plate until charring and partial ashing have occurred. Complete the ashing at 550 to 600° C in an electric furnace reserved for the ignition of low fluoride materials. The ash should be white or gray, indicating removal of organic matter.

2.4.4 When the ash has cooled, pulverize it and scrape all material from the dish, mix and determine the net wt. Store in a tightly stoppered bottle.

2.4.5 In order to effect quantitative release of fluoride combined with silica in many varieties of vegetation, fusion of the ignited ash with sodium hydroxide is required and is routinely performed on all vegetation specimens (**15, 18**). Transfer approximately one g of ash into a tared nickel, Inconel, or platinum crucible and weigh accurately. Add about 5 g of sodium hydroxide pellets, cover the vessel and fuse the contents for a few min over a gas burner. After cooling the melt note its color; a blue-green color indicates the presence of manganese and treatment with hydrogen peroxide is required as described under *Procedure for Single Distillation, Vegetation Ash*. Disintegrate the melt with hot water, washing down the lid and walls of the crucible. Reserve the resulting material for isolation of fluoride.

[9] Inconel dishes 14 cm in diam and 8 cm high, obtainable from Precision Metal Spinning Company, 2925 Dixie Highway, Clarkston, Michigan, are satisfactory.

PART B: *Isolation of Fluoride (Willard-Winter Distillation)*

1. Principle of the Method

The prepared sample is distilled from a strong acid such as sulfuric or perchloric, in the presence of a source of silica. Fluoride is steam-distilled as the fluosilicic acid under conditions permitting a min of volatilization and entrainment of the liberating acid (**1**).

2. Range and Sensitivity

The Willard-Winter distillation method, on the macroscale, can accommodate quantities of fluoride ranging from 100 mg down to a few µg.

3. Interferences

Samples relatively free of interfering materials, and containing fluoride in forms from which it is easily liberated, may be subjected to a single distillation from perchloric acid at 135° C. Samples containing appreciable amts of aluminum, boron, or silica require a higher temp and larger volume of distillate for quantitative recovery. In this case a preliminary distillation from sulfuric acid at 165° C is commonly used. Traces of chloride are separated by precipitation with silver perchlorate following the first distillation. Small amts are held back in the second distillation from perchloric acid by addition of silver perchlorate solution to the distilling flask.

4. Precision and Accuracy

Recovery data for the Willard-Winter distillation, as given in the literature, are difficult to dissociate from inaccuracies inherent in various methods of sample preparation and final evaluation of fluoride. Recovery data from field samples are further complicated by variability of interfering substances and ranges of fluoride contained. In general, recoveries should be within ± 10 per cent of the amt of fluoride present. Under favorable circumstances of sample composition and fluoride range, mean recoveries of approximately 99 per cent with standard deviation of about 2.5 per cent, have been reported (**20**).

5. Apparatus

5.1 *Steam Generator* (Figure 1) — 2000-ml Florence flask made of heat-resistant glass. Each flask is fitted with a stopper having at least 3 holes for inserting 6-mm OD heat-resistant glass tubing. Through one of the glass tubes, bent at right angles, steam is introduced into the distilling flask. The second tube is a steam release tube (Fig. 1D) which controls the steam pressure. The small piece of rubber tubing which is slipped over the end of the steam release tube is clamped shut during sample distillation. The third tube is a safety tube. If desired, other tubes may be added to permit the steam generator to supply a series of 3 distilling flasks. Any suitable boiling device may be used.

5.2 *Distilling Flask* (Figure 1E) — A 250-ml modified Claisen flask made of heat-resistant glass. The auxiliary neck of this flask is sealed and the outer end of the side tube is bent downward so that it may be attached to an upright condenser. The side tube is fitted with a one-hole rubber stopper to fit the condenser and main neck with a two-hole stopper through which pass a thermometer and a 6-mm OD heat-resistant glass inlet tube for admitting the steam. Any suitable heating device may be used.

5.3 *Tube Condenser* (Figure 1C) — heat-resistant glass, 300-mm jacket.

5.4 *Steam Release Tube* (Figure 1D) — (See *Steam Generator*, Section 5.1.)

5.5 *Thermometer* (Figure 1F) — Partial-immersion thermometer having a range of 0 to 200° C.

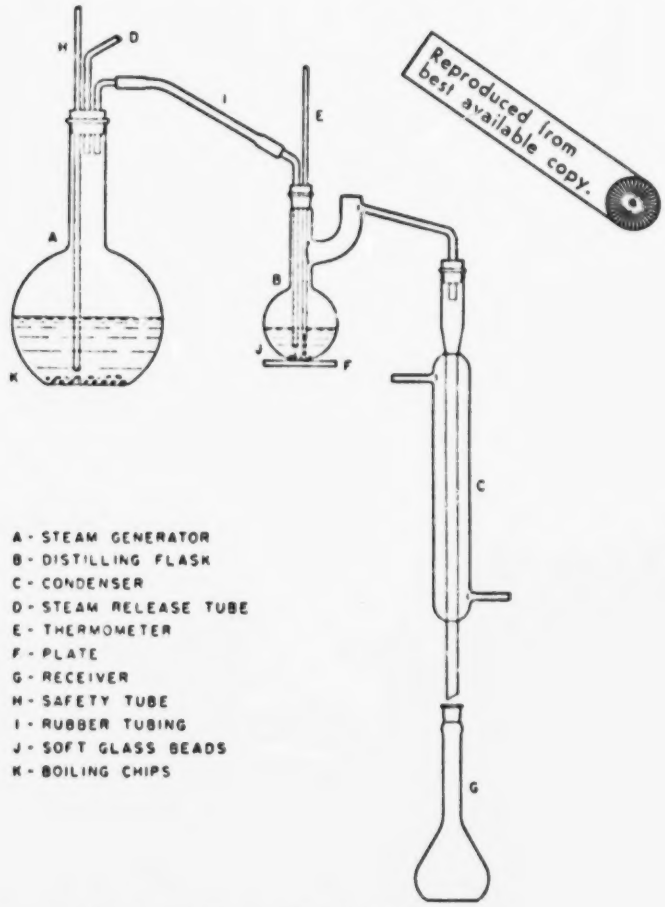
5.6 *Support Plate* (Figure 1G) — metal, ceramic, or hard asbestos board. The plate shall have a perfectly round 5-cm hole in which the distilling flask is placed as shown in Figure 1. The Claisen flask must fit well in the 5-cm hole so that the flask wall, above the liquid level, is not subjected to direct heat. Excessive heat on the wall of the flask causes the liberating acid to be distilled.

5.7 *Receiver* (Figure 1G) — 250- or 500-ml volumetric flask, or 400-ml beaker.

5.8 *Safety Tube* (Figure 1H) — A 6-mm OD heat-resistant glass tubing, 60-

cm long, one end of which is 1 cm from the bottom of the steam generator flask.

5.9 *Rubber Tubing* (Figure 1, I)—for flask connections, made from natural rubber. Lengths of rubber tubing shall be kept as short as possible.



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A - STEAM GENERATOR
B - DISTILLING FLASK
C - CONDENSER
D - STEAM RELEASE TUBE
E - THERMOMETER
F - PLATE
G - RECEIVER
H - SAFETY TUBE
I - RUBBER TUBING
J - SOFT GLASS BEADS
K - BOILING CHIPS

Figure 1—Apparatus for distillation of fluoride.

5.10 *Soft Glass Beads* (Figure 1, J)—Accordion for use in the distilling flask to prevent superheating and to supply sites for the formation of fluosilicic acid during distillation.

5.11 *Porous Porcelain Stones or Boiling Chips* (Figure 1, K).

5.12 *Perchloric* (Figure 1, I)—to control steam supply from the generator.

6. Reagents

6.1 *Perchloric Acid*—(70–72 per cent by wt)—Concentrated perchloric acid ($HClO_4$).[1]

6.2 *Silver Perchlorate Solution*—(50 per cent w/v)—Dissolve 100 g of silver perchlorate ($AgClO_4$) in 100 ml of water.

6.3 *Sulfuric Acid*—(96 per cent by wt)—Concentrated sulfuric acid (H_2SO_4).[1]

6.4 *Water*—All references to water shall be understood to mean distilled or deionized water of reagent purity.

7. Procedure

7.1 *Procedure for Single Distillations, Miscellaneous Materials*

7.1.1 Fill a steam generator about two-thirds full of water. Add to it a pellet of sodium hydroxide and a few drops of phenolphthalein indicator solution to insure that the water remains alkaline at all times. Add a piece of pumice to prevent bumping, and heat the water to boiling. Keep the steam release tube open at this time and place a pinchcock on the steam supply tubing.

7.1.2 Introduce the sample into a Claisen distilling flask containing four or six glass beads. Wash down the sides of the flask with water and bring the volume to 50 to 75 ml, the lesser volume being more desirable. Insert in the main neck of the flask the rubber stopper that contains the thermometer and steam inlet tube. Set the flask in the 3-cm diam hole in the plate and connect the outlet to a receiver.

7.1.3 Rinse the sides of the beaker or crucible which contained the sample with 50 ml of perchloric acid (70 to 72 per cent) and add 1 ml of silver perchlorate. Transfer the rinsings to the distilling flask by means of a small funnel attached to the steam inlet tube. Rinse the beaker or crucible with water and add the rinsings to the flask. Mix the contents of the flask by gentle shaking and attach the flask to the steam generator. Place a 250-ml volumetric flask under the condenser to receive the distillate and begin heating the solution in the flask. Keep the pinchcock in place on the steam inlet tube until the contents of the distilling flask reach 145 °C.

7.1.4 Remove the pinchcock on the steam inlet tube and place it on the steam release tube of the steam generator. Maintain the distillation period (1 to 2 h) until the contents of the distilling flask frequently fo outgo deposition on the flask walls or excessive foaming that might retain fluoride. After collecting 250 ml of distillate during a period of about 1 h, remove the pinchcock from the steam release tube and place it on the steam inlet tube. Disconnect the rubber tubing from the steam inlet tube, and discontinue heating.[1]

Caution. When using perchloric acid, the usual precautions should be taken. Hot fuming perchloric acid may react explosively with reducing substances, such as organic matter. Therefore, it is well to see that any organic matter in the sample is destroyed in the ashing process prior to distillation. Precautions for the use of perchloric acid are available in Chemical Safety Data Sheet SD-11, Perchloric Acid Solutions, published by the Manufacturing Chemists Association of the United States (11).

Caution. The distilling flasks should be cleaned using only a brush and distilled water. Repeated use of alkaline cleaning solution produces an etched surface that is difficult to clean and tends to retain fluoride.

[1] Acid giving excessively high fluoride blanks requires preboiling at 155° C, with admission of steam, prior to addition of samples.

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7.2 *Procedure for Single Distillation, Vegetation Ash*

7.2.1 Transfer the disintegrated melt to a Claisen distilling flask as described in section 7.1 for Miscellaneous Materials.

7.2.2 Rinse the sides of the crucible in which the fusion was made with 50 ml of perchloric acid (70 to 72 per cent) and add 1 ml of silver perchlorate solution.

7.2.3 If the sample contains manganese, add sufficient (2 to 10 drops) 3 per cent hydrogen peroxide solution to the contents of the distilling flask to reduce manganese dioxide and permanganates (6).

7.2.4 Carry out the distillation as previously described, except that a 500-ml volumetric flask is used as receiver and filled with distillate during a period of about 2 hr.

7.3 *Procedure for Double Distillation*

7.3.1 Fill a steam generator, as directed under *Procedure for Single Distillation*. Transfer the sample solution to a Claisen flask and rinse the sides of the beaker or crucible which contained the sample with 50 ml of cooled sulfuric acid. Transfer the rinsings to the distilling flask through a small funnel attached to the steam inlet tube. Mix the contents of the flask by swirling, rinse and remove the funnel, and connect the distilling flask to the steam generator. Place a 400-ml beaker under the condenser and begin heating the distilling flask and steam generator. Keep the pinchcock in place on the steam inlet tube until the contents of the distilling flask reach 165° ± 5° C. Swirl contents of the flask as required to prevent accumulation of insoluble material on the walls of the flask above the liquid level. Collect about 175 ml of distillate during a period of about 1½ to 2 hr.

7.3.2 Add sodium hydroxide solution (40 g/liter) to the distillate until alkaline by phenolphthalein indicator. Evaporate the distillate to 10 to 15 ml by heating below the boiling point.

7.3.3 The concentrated distillate is redistilled from perchloric acid as directed under *Procedure for Single Distillation*. Small quantities of chloride are fixed in the distilling flask by the addition of 1 ml of silver perchlorate solution. A 250-ml quantity of distillate is collected in a volumetric flask.

8. Calibration and Standards

9. Calculation

10. Effect of Storage

11. References (See Part VI, Section 11.)

C.

PART III: *Isolation of Fluoride (Ion Exchange)*

1. Principle of the Method

The sample is freed of interferences by preferential sorption on an ion exchange resin, followed by desorption of fluoride in a small volume of eluting solution. Thus, concentration of fluoride from impinger- or bubbler-collection media may be achieved without the attendant danger of contamination on prolonged exposure of solutions during evaporation (12).

2. Range of Sensitivity

The ion exchange procedure can be adapted to quantities of fluoride in the low-mg to μg range.

3. Interferences

Interfering anions may be eliminated by sorption of fluoride on an anion exchange resin. Fluoride is then eluted with sodium hydroxide solution.[1]

4. Precision and Accuracy

Net corrections for quantities of fluoride of 20 μg or more should be within ± 5 per cent of the quantity present. Low recovery indicates incomplete preconditioning of a new column, while high recovery may be due to contamination or failure to elute completely the previous sample.

5. Apparatus

5.1 *Chromatographic Column*. Dimensions of the column are not critical and many types, available from suppliers' stocks, are usable. A column made of borosilicate glass tubing 10 mm ID and 16 cm long, having a bulbed glass disc fused into the constricted base, and a reservoir of about 100 ml capacity at the top, is satisfactory. A short piece of polyvinyl chloride tubing attached to the bottom and closable with a screw hose clamp permits adjustment of flow rates and provides complete drainage of liquid from the column.

5.2 *Quartz Sand, Rinse*. Sand of −60 + 120 mesh, purified by hot extraction with 20 per cent sodium hydroxide solution, followed by hot 10 per cent hydrochloric acid solution, is used as a protective layer at the top of the resin bed.

6. Reagents

6.1 *Anion Exchange Resin*, Intermediate-Base of the granular aliphatic polyamine type:

- Duolite A-41, A-43 (Diamond Alkali Co.)
- Ionac A-302 (Ionac Chem. Co., Div. of Ritter Pfaudler Corp.)
- Permutit A (Permutit Co., Ltd., Div. of Ritter Pfaudler Corp.)
- Rexyn 205 (OH) (Fisher Scientific Co.)

Mesh size is not critical but, along with column diameter and height, is a factor in controlling flow rate of solutions. Mesh sizes of −40 + 100 or −100 + 200 are usable.[2]

6.2 *Hydrochloric Acid*, 2.0 N and 1.0 N solutions.

6.3 *Sodium Hydroxide*, 2.0 N, 0.1 N, and 0.01 N solutions.

7. Procedure

7.1 Prepare the resin column by adding a few ml of water to the chromatographic tube, then a slurry of resin (1:1 in water). Add sufficient slurry so that when the resin has settled, a layer 10 to 12 cm in height will result. Level the resin bed by twirling the tube, and before the water level has dropped below the surface of the resin, add a 2-cm layer of quartz sand. Wash the resin with 200 ml of 2.0 N hydrochloric acid solution, rinse with water, wash with 200 ml of 2.0 N sodium hydroxide solution, and finally, rinse with 200 ml water.

7.2 Precondition the resin by passing 100 ml of a solution containing about 1 ppm hydrofluoric acid and an equal volume containing 1 ppm sodium fluoride through the column at a rate of about 5 ml/min. Follow this with 50 ml of 0.1 N sodium hydroxide solution, then 25 ml of 0.01 N sodium hydroxide

[1] When interferences are present in cationic as well as anionic forms, both may be removed by use of a strongly basic anion exchange resin. This is accomplished by conversion of cations into strongly held complex anions, while the weakly held fluoride ions are quantitatively eluted from the column (10).

[2] Separation of fluoride may be achieved with other resins and appropriate eluting solutions; for example, Dowex 1X8 in the acetate form may be used with elution by sodium acetate solution (11).

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solution. Discard the eluate. The resin is now ready for use.

7.3 Acidify the sample solution by addition of 0.5 ml of 1 N hydrochloric acid per 100 ml, but add no more than 3 ml of 1 N hydrochloric acid per sample. Remove, by filtration, any solids remaining in the sample after acidification. Pass the sample solution through the resin column at a rate of about 10 ml/min, followed by a water rinse of a few ml. Elute fluoride with a 25-ml portion of 0.1 N sodium hydroxide solution, followed by a 25-ml portion of 0.01 N sodium hydroxide solution.

8. Calibration and Standards

9. Calculation

10. Effect of Storage

An ion exchange column may be preserved indefinitely if the resin is covered with water. Before the column is reused, a recovery test should be made by passage of a measured quantity of standard fluoride solution through the column; 200 ml of neutral sodium fluoride solution, at a rate of 10 ml/min, is suggested. The quantity of fluoride added should approximate that expected in the sample. Fluoride is eluted, as described under *Procedure*, and determined by the method selected for evaluation of samples.

11. References (See Part VI, Section 11.)

D.

PART IV: *Isolation of Fluoride (Diffusion)*

1. Principle of the Method

An aliquot of the prepared sample is mixed with a strong acid, gently heated in a sealed container, and the liberated hydrogen fluoride is absorbed by an alkali (7,17,19).

2. Range and Sensitivity

Quantities of fluoride from about 30 μg to a few tenths of a μg may be used. In routine work, blanks range from 0.5 μg to 0.0 μg.

3. Interferences

Interfering materials that volatilize from acid medium must be eliminated. Sulfites are oxidized to sulfate by preliminary treatment with 30 per cent hydrogen peroxide solution. Relatively large amts of chloride may be fixed in the diffusion vessel as silver chloride, by addition of 0.1 to 0.2 g silver perchlorate to the sample aliquot prior to diffusion. Samples high in carbonates require caution upon acidification, to control effervescence.

4. Precision and Accuracy

Recoveries from five sodium fluoride standards, covering the range 4 μg to 20 μg F, varied from 97.5 per cent to 102.5 per cent; average 99.4 per cent (17). By a slightly modified technic, standards containing 0.2 μg, 0.5 μg, and 1.0 μg F (five replicates of each) yielded recoveries of 94 per cent to 101 per cent; average 98.1 per cent (7).

5. Apparatus

5.1 *Microdiffusion Dish*—Disposable plastic Petri dish, 43 mm ID by 8 mm deep. (Obtainable from Millipore Filter Corp., Bedford, Mass. 01730).[6]

[6] The Conway Microdiffusion Dish, with Obrink modification, made of methyl methacrylate resin or similar plastic capable of withstanding temps up to 60° C, may also be used.

5.2 *Oven*—A thermostatically controlled oven capable of maintaining temp with ± 1° C in the 50° to 60° C range.

5.3 *Pipet, Mohr*—Capacity 0.1 ml, 0.01 ml subdivisions.

6. Reagents

6.1 *Perchloric acid*, 70 to 72 per cent.[7]

6.2 *Silver perchlorate*, anhydrous, C.P., ($AgClO_4$).

6.3 *Sodium hydroxide*, 1 N alcoholic solution—Dissolve 4 g sodium hydroxide (NaOH) in 5 ml of water and dilute to 100 ml with ethyl-, methyl- or Formula 30 denatured alcohol.

7. Procedure

7.1 Place 0.05 ml of 1 N alcoholic sodium hydroxide solution on the center of the inside top of the plastic Petri dish. Use the tip of the 0.1-ml Mohr pipet to spread the droplet into a circular spot of about 3-4 cm diam. Dry the top for about 1 hr, under slightly reduced pressure, in a desiccator containing activated alumina.

7.2 Transfer a 1.0 ml aliquot of prepared sample solution to the diffusion unit. Add 2.0 ml of perchloric acid and immediately close the dish with a prepared lid. Place the unit in an oven maintained at the selected temp (50° to 60° C) and allow to remain for 16-20 hr.

7.3 Carefully remove the diffusion vessel from the oven and take off the lid. Wash the alkaline absorbent into a 10- or 25-ml volumetric flask (a small funnel is helpful), the size of the flask depending upon amt of fluoride expected and method of measurement chosen.

8. Calibration and Standards

9. Calculation

10. Effect of Storage

11. References (See Part VI, Section 11.)

E.

PART V: *Determination of Fluoride (Titrimetric Methods)*

1. Principle of the Method

1.1 In the direct titration of fluoride with standard thorium nitrate solution, the sample solution or distillate containing sodium alizarinsulfonate is buffered at pH 3.0. Upon addition of thorium nitrate, insoluble thorium fluoride is formed. When the endpoint is reached, and all fluoride has reacted, the addition of another increment of thorium nitrate causes formation of a pink "lake" (16).

1.2 In the back titration procedure, the pink lake is first formed by addition of sodium alizarinsulfonate and a slight excess of thorium nitrate to the sample. Equal amounts of dye and thorium solution are added to a fluoride-free reference. The reference solution is then titrated with standard sodium fluoride solution until a color match is achieved with the unknown sample (16).

2. Range and Sensitivity

The direct titration procedure can accommodate 10 to 0.05 mg fluoride in the total sample. The back titration modifications can measure 50 to about 5 μg fluoride in the total sample. With photometric endpoint detection, direct titration can also be used for the lower ranges.

3. Interferences

3.1 Ions capable of forming insoluble or undissociated compounds with fluorine or with thorium interfere with

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these titrimetric methods and must be separated by an appropriate technic (eg distillation, diffusion or ion exchange). Among the more common of the interfering cations are Al^{+3}, Ba^{+2}, Ca^{+2}, Fe^{+3}, Th^{+4}, TiO_2^{+2}, VO^{+2}, and Zr^{+4}. The principal interfering anions are PO_4^{-3} and SO_4^{-2}. However, any material which constitutes an appreciable change in total ionic strength of the sample solution will affect the endpoint color as well as stoichiometry of the reaction. Thus, excessive acidity in the distillate from a Willard-Winter distillation, as from the liberating acid or chloride content of the sample, will interfere. This effect may be reduced by careful control of temp and rate of admission of steam, and by separation of chloride. Similarly, acidity or alkalinity of eluates from ion exchange separations must be matched with that of standards used in calibration, and with the requirements of the method of evaluation.

3.2 Sulfide and sulfite interferences are prevented by preliminary oxidation with 30 per cent hydrogen peroxide in boiling solution, as described under *Sample Preparation*. Interference by free chlorine is eliminated by addition of hydroxylamine hydrochloride solution.

4. Precision and Accuracy

5. Apparatus

5.1 *Fluorescent Lamp* - to provide illumination for titrating.

5.2 *Microburet* - having 5-ml capacity, 0.01-ml divisions, and a reservoir holding about 50 ml.

5.3 *Nessler Tubes* - Matched set of 50-ml, tall-form tubes with shadowless bottoms. Tubes may be fitted with either ground glass or rubber stoppers. The set should be checked for optical similarity as follows: Add to the tubes 40 ml of water, 1 ml of sodium alizarinsulfonate solution, and 2 ml of 0.05 N hydrochloric acid. Add thorium nitrate solution from a buret until the color of the solution just changes to pink. Close the top of the tube and invert several times. Add the same quantity of thorium nitrate solution to the remaining tubes. Fill all the tubes to the 50-ml mark with water and mix. Compare the colors and reject any tubes showing differences in shade or intensity.

5.4 *Nessler Tubes* Matched set of 100-ml, tall-form tubes with shadowless bottoms. The set should be checked for optical similarity, using the same technic as with the 50-ml tubes, except that the quantities of reagents shall be doubled.

5.5 *Nessler Tube Rack or Comparator*.

5.6 *Photometric Titrator* A Beckman Model B Spectrophotometer, equipped with an Alcoa Research Laboratories' titration attachment (Figure 2) or equivalent (3). Light from the monochromator passes through a 20.3-cm (8-inch) sample cell to the blue-sensitive phototube mounted at the outboard end of the cell housing. A magnetic stirrer is attached under the cell compartment. The tip of a semimicroburet passes through the cell housing and is immersed in the solution to be titrated. A ball-and-socket joint connects the tip to the buret, facilitating removal of the sample cell. The titration cell is 5.1 cm (2 inches) wide, 7.6 cm (3 inches) deep, and 20.3 cm (8 inches) long.

6. Reagents

6.1 *Buffer-Indicator Solution* - Dissolve 0.40 g of sodium alizarin-sulfonate in about 200 ml of water. Weigh 47.25 g of monochloracetic acid into a 600-ml beaker and dissolve in 200 ml of water. Add indicator solution with stirring. Dissolve 10 g of sodium hydroxide pellets in 50 ml of water, cool to approximately 15° to 20° C, and add to the above solution slowly with stirring.

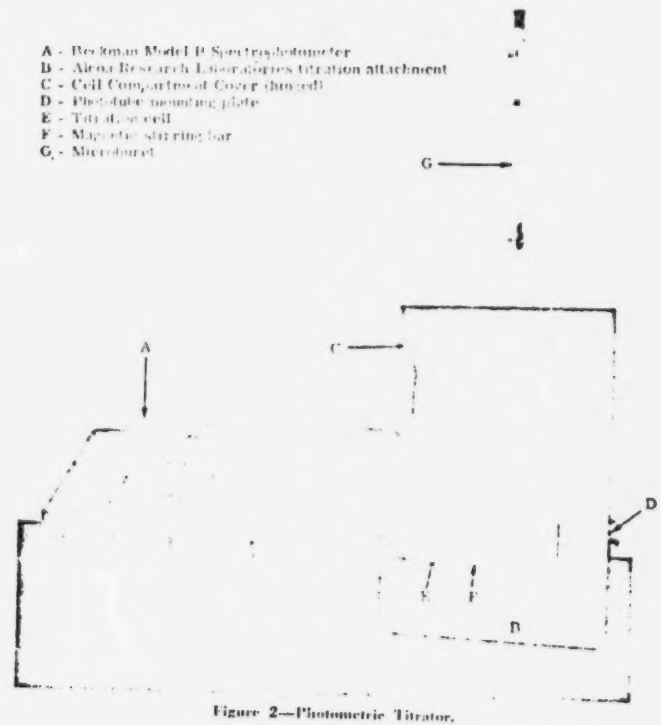

Figure 2—Photometric Titrator.

Filter and make to 500 ml. Prepare fresh weekly.

6.2 *Chloroacetate Buffer Solution* — Dissolve 9.45 g of monochloroacetic acid and 2.0 g of sodium hydroxide (NaOH) in 100 ml of water. This solution is stable for more than two weeks if stored under refrigeration.

6.3 *Hydrochloric Acid, Standard Solution* (0.05 N) — Dilute 4.28 ml of hydrochloric acid (HCl, sp gr 1.19) to 1 liter. The normality of this solution should be exactly equal to that of the sodium hydroxide (NaOH) solution (0.05 N).

6.4 *Hydroxylamine Hydrochloride Solution* - 1 g of $NH_2OH.HCl$ 100 ml of water.

6.5 *Phenolphthalein Indicator Solution* (0.5 g liter) — Dissolve 0.5 g of phenolphthalein in 60 ml of ethyl alcohol and dilute to 1 liter with water.

6.6 *Sodium Alizarinsulfonate Solution* (0.80 g liter) — Dissolve 0.40 g of

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sodium alizarinsulfonate in 500 ml of water.[7]

6.7 *Sodium Alizarinsulfonate Solution* (0.01 g liter)—Dissolve 0.01 g of sodium alizarinsulfonate in 1000 ml of water.

6.8 *Sodium Fluoride, 100 Per Cent.*

6.9 Sodium Fluoride, Standard Solution (1 ml = 1.00 mg F)—Dissolve 2.2105 g of sodium fluoride (NaF, 100 per cent) in water and dilute to 1 liter in a volumetric flask, mix, and transfer to a polyethylene bottle for storage.

6.10 *Sodium Fluoride, Standard Solution (1 ml = 0.01 mg F)*—Dilute 10 ml of NaF solution (1 ml = 1.00 mg F) to 1 liter with water in a volumetric flask, mix, and transfer to a polyethylene bottle for storage.

6.11 *Sodium Hydroxide Solution (10 g liter)*—Dissolve 10 g of NaOH in water, dilute to 1 liter and mix. Store in a polyethylene bottle.

6.12 *Sodium Hydroxide, Standard Solution (0.05 N)*—Dissolve 2.00 g of NaOH in water and dilute to 1 liter. The normality of this solution should be exactly equal to that of the standard HCl (0.05 N). Store in a polyethylene bottle.

6.13 *Thorium Nitrate, Standard Stock Solution (1 ml = 1.9 mg F)*—Dissolve 13.30 g of thorium nitrate tetrahydrate ($Th(NO_3)_4 \cdot 4H_2O$) in water and dilute to 1 liter.

6.14 *Thorium Nitrate Solution (0.25 g liter)*—Dissolve 0.25 g of thorium nitrate tetrahydrate ($Th(NO_3)_4 \cdot 4H_2O$) in water, dilute to 1 liter and mix. Store in a polyethylene bottle.

6.15 *Thorium Nitrate Solution, 0.01 N (0.19 g F liter)*—Dilute a 100-ml aliquot of the stock solution (6.13) to 1 liter and store in a polyethylene bottle.

[7] In the literature, this reagent is also known as alizarin Red S, alizarin Red, alizarin S, alizarin carmine, alizarin, sodium alizarin sulfonate, sodium alizarin monosulfonate, monosodium alizarin sulfonate, and 3-alizarinsulfonic acid sodium salt. The dye is identified by Color Index No. 58005.

7. Procedure

7.1 *Procedure for Direct Titration, High Concentrations* (10 to 0.05 mg F in Total Sample).

7.1.1 Pipet an aliquot of the distillate into a 100-ml beaker and dilute to 100 ml. Add 1 ml of sodium alizarinsulfonate solution (0.30 g liter), and then sodium hydroxide solution (10 g liter) dropwise until a pink color is obtained. Discharge the pink color by adding 0.05 N hydrochloric acid dropwise. Add 1 ml of chloroacetate buffer solution dropwise, and titrate with thorium nitrate solution (1 ml = 1.9 mg F) to a faint, persistent, pink endpoint. Determine a blank obtained by carrying the same amt of all reagents through the entire procedure.

7.2 *Procedure for Back Titration, Medium Concentration* (0.05 to 0.01 mg F in Total Sample).

7.2.1 Transfer 50 ml of the distillate into a 50-ml Nessler tube, add 1 ml of sodium alizarinsulfonate solution (0.01 g liter) and sufficient 0.05 N sodium hydroxide solution to produce a pink color. Note precisely the volume of 0.05 N sodium hydroxide solution required for neutralization; then discard the titrated solution. If more than 4 ml of 0.05 N sodium hydroxide solution is required, make the remaining distillate alkaline, evaporate to 10 to 15 ml, and transfer it to a distilling flask. Repeat the distillation, precautions being taken to reduce the amt of perchloric acid distilled over.

7.2.2 Transfer another 50-ml portion of distillate into a 50-ml Nessler tube (sample tube) and add 1 ml of sodium alizarinsulfonate solution (0.01 g liter). Adjust the acidity with 0.05 N hydrochloric acid until the equivalent of exactly 2 ml of acid is present; that is, 2 ml minus the number of ml of 0.05 N sodium hydroxide solution required for neutralization as described. If between 2 ml and 4 ml of 0.05 N sodium hydroxide solution were required for neutralization, omit the addition of hydrochloric acid to the distillate. Add thorium nitrate solution (0.25 g liter) from a microburet until a faint pink color appears. Note the volume of thorium nitrate solution required, and save the Nessler tube for comparison with the standard.

7.2.3 Pour 50 ml of water into a 50-ml Nessler tube (standard tube) and add 1 ml of sodium alizarinsulfonate solution of (0.01 g liter). If neutralization of the sample requires 2 ml or less of 0.05 N sodium hydroxide solution, pipet exactly 2 ml of 0.05 N hydrochloric acid into the standard tube. If the 50-ml aliquot of the distillate requires more than 2 ml of 0.05 N sodium hydroxide solution for neutralization, no further acidification of the distillate is necessary, but add to the standard tube a quantity of acid equivalent to that found in the sample distillate.

7.2.4 From a microburet add sodium fluoride solution (1 ml = 0.01 mg F) equivalent to about 50 per cent of the fluoride present in the sample aliquot, as indicated by the thorium nitrate solution required. Mix thoroughly, add the same volume of thorium nitrate solution as that required for titration of the sample aliquot as described, and again mix thoroughly. The color in the standard tube will be deeper than that in the sample tube.

7.2.5 From the microburet continue to add sodium fluoride solution (1 ml = 0.01 mg F) to the standard tube until its color matches that of the sample tube. (If the colors cannot be matched repeat the distillation.) Equalize the volumes in the sample and standard tubes by adding water. After the addition of water, mix thoroughly, then allow all bubbles to escape before making the final color comparison. Check the end point by adding 1 or 2 drops of sodium fluoride solution (1 ml = 0.01 mg F) to the standard tube. If the colors were originally matched the color in the standard tube will be distinctly lighter in shade than that in the sample tube.

7.2.6 Determine a blank by carrying the same amt of all reagents through the procedure described. With proper attention to detail, blanks of 5 μg of fluoride or less can be obtained.

7.3 *Procedure for Back Titration, Low Concentrations* (less than 0.01 mg F in Total Sample).

7.3.1 Distill successive 5 to 50-ml portions of distillate directly into three or four 100-ml Nessler tubes. Take care to keep the amt of perchloric acid distilling over as small as possible, because the entire distillate is titrated and there is no aliquot available for a separate acidity determination. Analyze each of the distillate portions in the 100-ml Nessler tubes separately as follows:

7.3.1.1 Add 2 ml of sodium alizarinsulfonate solution (0.01 g liter) and neutralize the acid by adding 0.05 N sodium hydroxide solution until a pink color is produced. Add 1 ml of 0.05 N hydrochloric acid and sufficient thorium nitrate solution (0.25 g liter) to provide a faint pink color. Compare the treated distillate portion with a standard of equal total volume containing 2 ml of sodium alizarinsulfonate solution (0.01 g liter), 1 ml of hydrochloric acid and the same volume of thorium nitrate solution (0.25 g liter) as is required to produce the pink color in the sample tube. Add sodium fluoride solution to the standard tube until the color matches that of the sample tube. The sum of all significant amts of fluoride found in each successive portion of distillate is the total amt of fluoride in the sample.

7.4 *Procedure for Photometric Titration*—

7.4.1 Transfer the distillate to a 20.3 cm (8-inch) titration cell and add 5 ml of hydroxylamine hydrochloride

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solution. Adjust, if necessary, to pH 3.6 with 0.05 N perchloric acid, and then add 5 ml of buffer-indicator solution.[8]

7.4.2 Place the cell in the titrating attachment, immerse the buret tip, and start the stirring motor. Close the titrator lid, set the wavelength to 525 mμ, and the sensitivity knob to the proper position (usually 1). Close the shutter and adjust the slit width to give a transmittance reading of 100.

7.4.3 Titrate with standard thorium nitrate (0.01 N solution) to a transmittance reading of 75 per cent. Record the volume to the nearest 0.005 ml.

7.4.4 Deduct a blank obtained by carrying the same amt of all reagents through the entire procedure, including the preliminary distillation and titration steps. Determine the amt of fluoride present from the calibration chart.

8. Calibration and Standards

8.1 *Thorium Nitrate, Standard Stock Solution* (1 ml = 1.9 mg F). Standardize this solution as follows:

8.1.1 Weigh 0.100 g of sodium fluoride into a distilling flask and collect 250 ml of distillate as previously described. Titrate 50 ml of the distillate (20 mg of NaF) with the solution being standardized. Carry a blank through the same procedure. Calculate the strength of the thorium nitrate solution in terms of mg of fluoride ion/ml of solution as follows:

$$\text{Fluoride ion, mg/ml} = \frac{C \times 20}{A - B}$$

Where:

A = ml of $Th(NO_3)_4 \cdot 4H_2O$ solution required for titration of the fluoride,

B = ml of $Th(NO_3)_4 \cdot 4H_2O$ solution required for titration of the blank, and

C = 0.4524 when titrating sodium fluoride (NaF).

8.2 *Thorium Nitrate Solution*, 0.01 N (0.19 g F/liter). Prepare a calibration curve for this solution from data obtained in the following way:

8.2.1 Pipet aliquots of standard sodium fluoride solution covering the range 10 to 1000 μg of fluoride into 500-ml volumetric flasks and dilute to volume. Transfer to a 20.3-cm titration cell, add 5 ml of hydroxylamine hydrochloride solution, and adjust to pH 3.6 with 0.05 N perchloric acid. Add 5 ml of buffer-indicator solution and titrate as described in the *Procedure for Photometric Titration*.

9. Calculation

9.1 Calculate the fluoride ion content of the total distillate[9] in mg as follows:

$$F = \frac{(A - B)CD}{E}$$

Where:

F = mg of fluoride ion in total distillate,

A = ml of titrating solution[10] used in titration of sample aliquot,

B = ml of titrating solution[10] used in titrating the blank,

C = fluoride equivalent of titrating solution[10] in mg of fluoride ion/ml of solution,

D = ml of total distillate collected,[9] and,

E = ml of distillate titrated.[9]

9.2 Calculate the fluoride concn in the atmosphere at 25° C and 760 torr, in terms of ppm of hydrogen fluoride (HF) or fluorine (F_2), or mg of particulate fluoride/m³, as follows:

$$\text{Hydrogen fluoride, ppm} = \frac{4140 \times F \times 0.273 + t}{PV}$$

$$\text{Fluorine, ppm} = \frac{1640 \times F \times 0.273 + t}{PV}$$

$$\text{Particulate fluoride, mg/m}^3 = \frac{2550 \times F \times 0.273 + t}{PV}$$

either the $Th(NO_3)_4$ solution used in accordance with the Procedure for Direct Titration, or the NaF solution (1 ml = 0.01 mg F) used in Procedure for Back Titration, Medium Concentration and in Procedure for Back Titration, Low Concentrations.

Where:

F = mg of fluoride ion in total sample

P = sampling pressure in torr (mm of mercury),

t = sampling temp in degree celsius, and

V = sample volume in liters.

9.3 Calculate the fluoride concn in vegetation on the oven-dry basis, as follows:

$$\text{Fluoride (ppm, dry basis)} = \frac{F \times A \times 1000}{W \times S \times [1 + (M/100)]}$$

Where:

F = mg of fluoride ion in total distillate,

A = g of total ash

W = g of ash distilled

S = g of fresh sample

M = percentage of moisture in fresh sample.

10. Effects of Storage

All reagent solutions listed are stable at room temp except as individually noted.

11. References (See Part VI, Section 11).

PART F: *Determination of Fluoride (Spectrophotometric Methods)*

1. Principle of the Method

Reaction of fluoride with the metal ion moiety of a metal-dye complex results in fading [Zirconium-Eriochrome Cyanine R (9) and Zirconium-SPADNS (4) reagents] or increase [Lanthanum-Alizarin Complexone (3) reagent] in the absorbance of the solution.

2. Sensitivity and Range

2.1 Both Zirconium-Eriochrome Cyanine R and Zirconium-SPADNS reagents obey Beer's Law over the range of 0.00 μg to 1.40 μg fluoride/ml with a detection limit of the order of 0.02 μg/ml. The procedure given for the lower-range, Lanthanum-Alizarin Complexone, covers the range 0.00 μg to 0.5 μg fluoride/ml with a detection limit of approximately 0.015 μg/ml.

2.2 In common with other spectrophotometric methods, these are temp sensitive and absorbances must be read within ± 2° C of the temp at which the respective calibration curve was established.

[8] The addition of buffer-indicator solution should adjust the pH to 3.0. For amts of fluoride ordinarily encountered, the pH of the distillate should be 3.5 to 3.7 if the distillation is properly controlled. The addition of buffer-indicator solution will maintain a pH of 3.0 under these conditions. For extreme cases, where acidity of the distillate is less than pH 3.5, 0.05 N sodium hydroxide may be used to raise the pH to the proper level. However, it has been found to be the rule that distillations properly conducted will have a pH greater than 3.5. The use of sodium hydroxide for neutralization produces a slight change in the factor due to the sodium perchlorate formed.

[9] The volume of total distillate collected normally is 250 ml. However, if any other volume of total distillate is collected, this volume shall be substituted for 250. The volume of the distillate titrated normally is 50 ml but may vary as described in *Procedure for Back Titration, Low Concentrations*. If this procedure applies, for each portion of distillate titrated, the value of E is equal to the value of D.

[10] The term "titrating solution" refers to

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3. Interferences

3.1 Moderate variations in acidity of sample solutions will not interfere with the *Zirconium-Eriochrome Cyanine R* or *Zirconium-SPADNS* reagents. The Lanthanum-Alizarin Complexone reagent has greater pH sensitivity and solutions must not exceed the capacity of the buffer system to maintain an apparent pH 4.50 ± 0.02.

3.2 Many ions interfere with these fluoride reagents, but those most likely to be encountered in analysis of ambient air are aluminum, iron, phosphate and sulfate. If these are present above the trace level their effects must be eliminated. Distillation, diffusion, or ion exchange may be employed but, in certain cases, complexation-extraction (2) may be advantageous.

3.3 In vegetation analysis, ashing and distillation by the Willard-Winter technic generally assure a sample solution sufficiently free of interfering ions for direct colorimetric evaluation. Traces of free chlorine in the distillate, if present, must be reduced with hydroxylamine hydrochloride.

4. Precision and Accuracy

Because of the wide variability in composition of samples, and in methods and conditions of sampling, no general statements of precision and accuracy for field samples can be given. Precision studies of pure sodium fluoride standards indicate that, within the concentration ranges for which the reagents follow Beer's Law, standard deviation of ± 0.015 to 0.020 μg of fluoride ion should be expected.

5. Apparatus

Spectrophotometer.—An instrument capable of accepting sample cells of 1 cm to 2.5 cm optical path, and which is adjustable throughout the visible wavelength region, is required. Each spectrophotometer sample cell is given an identification mark and calibrated by reading a portion of the same reagent blank solution at the designated wavelength. The determined cell correction is subsequently applied to all absorbance readings made in that cell.

6. Reagents

6.1 *Acetic acid*, glacial.

6.2 *Acetone*, reagent grade.

6.3 *Alizarin Complexone*, (1,2-dihydroxy-3-anthraquinonylamine-*N*, *N*-diacetic acid, available from Hopkins & Williams, Ltd., Chadwell Heath, Essex, England, cat. no. 130/4.)[11]

6.4 *Ammonium Acetate Solution* (20 per cent w/v).—Dissolve 20.0 g ammonium acetate in water and dilute to 100 ml.

6.5 *Ammonium Hydroxide*, sp gr 0.9[5]9

6.6 *Eriochrome Cyanine R Solution*.—Dissolve 1.300 g of Eriochrome Cyanine R (Mordant Blue 3, Color Index No. 14[6]20) in water to make 1 liter. Solution is stable for more than a year when protected from light.

6.7 *Lanthanum Chloride*, 99.9 per cent assay (Available from Kleber Laboratories, Burbank, Calif.)

6.8 *Lanthanum-Alizarin Complexone Reagent*.—Dissolve 8.2 g sodium acetate in 6 ml of glacial acetic acid, and sufficient water to permit solution, and transfer to a 200 ml volumetric flask. Dissolve 0.0479 g alizarin complexone in 1.0 ml of 20 per cent ammonium acetate solution, 0.1 ml ammonium hydroxide and 5 ml water. Filter this solution through a Whatman #1 paper into the 200 ml volumetric flask. Wash the filter with a few drops of water and discard the residue. Add 100 ml of acetone, slowly and with mixing, to the flask. Dissolve separately 0.612 g of lanthanum chloride in 2.5 ml 2 *N* hydrochloric acid solution, warming slightly to promote solution, and combine this with the flask contents.[12] Dilute, mix well, cool the solution to room temp and adjust the volume to the mark. The reagent solution is stable for about 1 week if kept under refrigeration.

6.9 *Sodium Fluoride Stock Solution* (1 ml = 1.0 mg F).—Dissolve 2.210[5] g of 100 per cent sodium fluoride, or the equivalent weight of reagent grade sodium fluoride, in water and dilute to 1 liter. Store in a polyethylene bottle.

6.10 *Sodium Fluoride Working Standard Solution* (1 ml = 10 μg F).—Dilute 5.0 ml of the stock solution to 500 ml. Store in a polyethylene bottle.

6.11 *SPADNS Solution* (4,5-dihydroxy-3-(*p*-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, available from Eastman Organic Chemicals, Rochester, N. Y., cat. no. 7300).—Dissolve 0.9[8]5 g SPADNS dye in water and dilute to 500 ml.

6.12 *SPADNS Reference Solution*.—Add 10 ml SPADNS Solution to 100 ml of water and acidify with a solution prepared by diluting 7 ml conc'd hydrochloric acid to 10 ml. This solution may be stored and reused repeatedly.

6.13 *Zirconium Solution*.—Dissolve 0.2[6]5 g of zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in 50 ml of water, add 700 ml of conc'd hydrochloric acid, and dilute to 1 liter with water.

6.14 *Zirconium-Eriochrome Cyanine R Reagent*.—Mix equal volumes of the Eriochrome Cyanine R and the zirconium solutions. Cool to room temp before use. Prepare fresh daily.

6.15 *Zirconium-SPADNS Reagent*.—Mix equal volumes of the SPADNS and the zirconium solutions. Cool to room temp before use. This reagent may be stored for several months, at room temp, in a polyethylene bottle.

7. Procedure

7.1 *Procedure for Intermediate Range*

7.1.1 **Zirconium-Eriochrome Cyanine R Reagent**.—Transfer an aliquot of the prepared sample, standard, or blank solution to a 25-ml volumetric flask containing 5 ml of the Zirconium-Eriochrome Cyanine R Reagent. Dilute the solution to the mark, mix well and allow to stand for 30 min for temp equilibration. Transfer the solution to a calibrated spectrophotometer cell of about 2.5 cm light path. The spectrophotometer is set on a wavelength of 5[6]0 nm and the light control adjusted to an absorbance value of 0.500 on a Reagent Blank-sample prepared.

7.1.1.1 Spectrophotometer cells of 1 cm to 5 cm path may be used by making the following adjustments of volumes: transfer the aliquot of sample, standard or blank solution to a 50 ml volumetric flask, and add 5 ml of Zirconium-Eriochrome Cyanine R Reagent. Dilute the mixture to the mark, mix well and allow to stand for 30 min, then read absorbance as previously described.

7.1.2 **Zirconium-SPADNS Reagent**.—Dilute a suitable aliquot of the sample solution to 25 ml and add 5.0 ml of Zirconium-SPADNS Reagent. Mix and allow to stand for 30 min to establish temp equilibrium before transferring the solution to a spectrophotometer cell (cells of 1 cm to 2.5 cm optical path may be used). Measure the absorbance value at 570 nm with the spectrophotometer adjusted to read zero absorbance on the SPADNS Reference Solution.

7.2 *Procedure, Lower Range*.—Lanthanum-Alizarin Complexone Reagent: Transfer a suitable aliquot of sample solution, containing no more than 4 μg of fluoride, to a 10 ml volumetric flask. Add 3 ml of Lanthanum-Alizarin Complexone Reagent, dilute to the mark and mix well. Allow to stand for 30 min. Measure the absorbance at 622 nm, in

[11] This reagent has been variously named in the literature, e.g. alizarin complexan, alizarin complexon, alizarin complexone, and alizarin Fluorine Blue.

[12] An equimolar concn of lanthanum nitrate may be substituted for the chloride.

a calibrated 1-cm cell, using a reagent blank as reference.

8. Calibration and Standards

8.1 *Zirconium-Eriochrome Cyanine R Reagent*—Prepare a standard series, spanning the range of zero to 20 μg of fluoride, by pipetting aliquots of the standard sodium fluoride solution (10 μg F/ml) into 25-ml volumetric flasks. Add 4 ml of Zirconium-Eriochrome Cyanine R Reagent to each flask, dilute to the mark and mix thoroughly. Allow the standards to stand until solution temp has equilibrated at the desired value. Measure absorbances at 536 nm, in 2.5-cm cells, against a reagent blank for which the spectrophotometer is adjusted to read 0.500 absorbance unit. Plot a calibration curve relating fluoride concn, in μg, to absorbance values at the selected working temp.

8.1.1 If 1-cm cells are to be used, a similar standard series is prepared in 10-ml volumetric flasks, adding 3 ml of Zirconium-Eriochrome Cyanine R Reagent to each flask, and reading as described above.

8.2 *Zirconium-SPADNS Reagent*—Prepare a standard series containing from zero to 35 μg of fluoride by pipetting aliquots of the standard sodium fluoride solution (10 μg F per ml) into 25-ml volumetric flasks. Add 5 ml of Zirconium-SPADNS Reagent to each flask, dilute to the mark and mix well. Allow the standards to stand 30 min to reach temp equilibrium at the desired value. Measure absorbances at 570 nm after zeroing the spectrophotometer on the SPADNS Reference Solution. Prepare a calibration curve relating fluoride concn, in μg, to absorbance values at the selected working temp.

8.3 *Lanthanum-Alizarin Complexone Reagent*—Prepare a standard series containing zero to 4 μg of fluoride by measuring portions of the standard sodium fluoride solution (10 μg F/ml) into 10-ml volumetric flasks. Add 3 ml of Lanthanum-Alizarin Complexone Reagent to each flask, dilute to the mark, mix and let stand for 30 min at the selected temp. Measure the absorbances at 622 nm in 1-cm cells, using a reagent blank as reference.

9. Calculation

Concentrations of fluoride in air or vegetation samples are calculated by use of the formulas given under *Part V: Titrimetric Methods*, Calculations 9.2 and 9.3.

10. Effects of Storage

Reagents used in these procedures are stable, except as individually noted.

11. References

1 *ASTM Standards on Methods of Atmospheric Sampling and Analysis*, 2nd Ed, Oct 1962

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C-13